THE NICKEL BULLETIN

A MONTHLY SUMMARY OF CURRENT INFORMATION

SEPTEMBER, 1957

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EFFECTS OF IMPURITIES IN NICKEL-PLATIN OLUTIO

(Based on Reports of the Americ ectropla

Impurity	Range Investigated (p.p.m.)*	Solution	Appearance	Adhesion	Ductility
Aluminium *Proc. A.E.S. 43rd Annual Convention*, 1956, pp. 44-6	0–100	Watts pH 2·2	Unaffected**	Unaffected	Unaffected
		Watts pH 5·2	Slight whitening at 10-100 p.p.m.		
		Co-Ni pH 3·75	Unaffected		
		Organic pH 3·2	Unaffected		
Calcium *Plating* 1957, vol. 44, Feb., pp. 186-7	>1000	Watts pH 2·2	Unaffected	Unaffected	Unaffected
	> 700	Watts pH 5·2			
	>1000	Co-Ni pH 3·75			
	>1000	Organic pH 3·2			
Chromium *Plating* 1953, vol. 40, Dec., pp. 1391-400	Chromium III				
	0–250	Watts pH 2·2	No effect up to 50 p.p.m.; thereafter deposits are smoother and finer-grained	Unaffected provided correct plating conditions, i.e., pH, were maintained	Decrease after 12·5-25 p.p.m.
	0–50	Watts pH 5·2	All deposits rough		Decrease after 5 p.p.m.
	0–250	Co-Ni pH 3·75	No effect up to 75 p.p.m.; thereafter organic deposits become milky and Co-Ni deposits become more highly stressed		Decrease after 50 p.p.m.
	0–125	Organic pH 3·2			Decrease after 25 p.p.m.
	Chromium VI‡				
	0–70	Watts pH 2·2	Whitens deposit	Unaffected if pH and Cr^{III} content are carefully controlled	9-16% decrease
	0–15	Watts pH 5·2	Deposits rough, due to Cr^{III} whitening of Cr^{III} precipitate		55-85% decrease
	0–40	Co-Ni pH 3·75	Unaffected		33-60% decrease
	0–35	Organic pH 3·2	Unaffected		25-50% decrease

* p.p.m. = parts per million.

** Deposits from all four types of solution showed pitting, which was alleviated by additions of wetting agent.

‡ In all tests with Cr^{VI} impurity some Cr^{III} was also present. The concentration of Cr^{III} was kept below 40 p.p.m.

lectroplaters' Society Research Project No. 5)

Hardness	Corrosion-Resistance in Salt-Spray Test	Throwing Power	Removal Technique
Slightly softened (min. at 50 p.p.m.)	Results erratic	Decrease (min. at 10 p.p.m.)	Cannot be removed by electrolysis. Aluminium is precipitated at pH above 4·5
Slightly variable		Decrease (min. at 20 p.p.m.)	
Softening, with increased Al concentration		Decrease (min. at 20 p.p.m.)	
Hardening (max. at 30 p.p.m.)		Slightly variable	
Unaffected	Unaffected	Unaffected	Cannot be removed by electrolysis, high-pH, high-temperature precipitation, or precipitation as fluoride
Decrease at all concentrations	General decrease in corrosion-resistance	Slight increase	Removal by electrolytic means is unsatisfactory
Increase with increasing concentration.		Slight increase	Reduction of Cr^{VI} to Cr^{III}, using nickel metal at low pH (<3·0) and agitating. Cr^{III} is removed by raising the temperature (to 75°C.) for several hours and precipitating at high pH (5·2-5·5), using nickel carbonate
Slight increase; max. at 12·5 p.p.m.)		Slight decrease	
Decrease (min. at 12 p.p.m.)		Slight increase	
Decrease at all concentrations	Substantial increase in thick deposits at high concentration; otherwise no great change.	Decrease	
Increase (43% at 15 p.p.m.)	As for pH 2·2 solution	Slight increase	
Mainly decrease but variable	Slight decrease at all thicknesses and concentrations	Slight decrease	
		Slight increase	

(*Continued on p.* 154.)

Impurity	Range Investigated (p.p.m.)*	Solution	Appearance	Adhesion	Ductility
Copper *Plating* 1950, vol. 37, Nov., pp. 1157-60	0–100	Watts pH 2·2 Watts pH 5·2 Co-Ni pH 3·75 Organic pH 3·2	50 p.p.m. causes blackening in low-current-density areas 10 p.p.m.—milky: higher concentration, deposits dull and rough	Unaffected up to 100 p.p.m.	Decreases as copper content increases above 10-25 p.p.m.
Iron *Plating* 1952, vol. 39, Dec., pp. 1343-9	0–200	Watts pH 2·2 Watts pH 5·2 Co-Ni pH 3·75 Organic pH 3·2	Whitens deposit at concentrations 10-200 p.p.m. Some brightness 50-200 p.p.m. Unaffected up to 200 p.p.m.	Unaffected up to 200 p.p.m.	Decreases at 25-50 p.p.m. Unaffected up to 200 p.p.m. Decreases at 25-50 p.p.m.
Lead *Plating* 1954, vol. 41, Nov., pp. 1307-11	0–15† 0–20 0–25 0–35	Watts pH 2·2 Watts pH 5·2 Co-Ni pH 3·75 Organic pH 3·2	Pronounced levelling and brightening effects even at low concentration Blackening in low-current-density areas at 20 p.p.m.; otherwise some levelling	Unaffected	Max. at 5 p.p.m. Min. at 15 p.p.m. General increase (50% at 20 p.p.m.) Unaffected Slight decrease (8% at 20 p.p.m.)
Manganese *Proc. A.E.S. 43rd Annual Convention* 1956, pp. 46-9	0–300	Watts pH 2·2 Watts pH 5·2 Co-Ni pH 3·75 Organic pH 3·2	Finer-grained and smooth Darkening in low-current-density areas above 80 p.p.m. Unaffected	Unaffected	Increase: max. at 80 p.p.m. Slight decrease Unaffected
Zinc *Plating* 1952, vol. 39, Sept., pp. 1033-7	0–300	Watts pH 2·2 Watts pH 5·2 Co-Ni pH 3·75 Organic pH 3·2	Darkening in low-current-density areas above 10 p.p.m. Brightening in high-current-density areas at 300 p.p.m. Darkening above 10 p.p.m. Gradual change to dull deposit at 300 p.p.m. Improved brightness at 150-300 p.p.m., but above 10 p.p.m. darkness in low-current-density areas	Unaffected up to 300 p.p.m.	Gradual decrease Little change until 300 p.p.m. at which concentration deposit becomes unusable Unaffected

* p.p.m. = parts per million.

† Higher concentrations of Pb are possible, especially in solutions containing organic additions and having a high chloride conte

Hardness	Corrosion-Resistance in Salt-Spray Test	Throwing Power	Removal Technique
Max. (+86%) at about 75 p.p.m.; less significant increases for other solutions	Small amounts cause large reduction in corrosion-resistance (50% reduction at 40 p.p.m. for all solutions)	Insignificant changes at all concentrations and in all solutions	Low-current-density, treatment, at 2 amp./ft.^{2} Ni : Cu ratio of deposit is twice that obtained at 1 amp./ft^2: at 3 amp./ft^2 it is 15 times as great High-pH treatment (pH 6·0) Cu reduced to 15 p.p.m. but with loss of nickel
Increase to max. at 10-25 p.p.m.; decreases to min. at 50 p.p.m. then increase again at higher concentrations	Slight changes only in thin deposits Unaffected 10-20% increase at 25 p.p.m. Slight changes only at all thicknesses	Insignificant changes	Oxidation with H_2O_2 (1% by volume of 3% H_2O_2) and high pH (5·5-5·7) with $NiCO_3$. No loss of nickel Also by low- or high-current-density treatment
Decrease Decrease Increase (12% at 10 p.p.m.) Decrease	General slight increase in corrosion-resistance especially in thicker deposits	General slight decrease Variable at different concentrations Slight increase	By low-current-density treatment (1 amp./ft.^{2}), to minimum of 2·5 p.p.m. By high-pH treatment (pH 5·5-6·0). (Some nickel also precipitated at the higher pH)
Slightly variable	Erratic results with thin deposits Thick deposits unaffected	Results variable Approx. 10% increase	Small amounts are removed electrolytically at about 60 amp./ft.^{2} Cannot be removed by high-pH treatment without much loss of nickel
General increase; greater at pH 2·2 than pH 5·2 Increase; max. at 25 p.p.m.	General improvement—greatest change in corrosion-resistance (10-60% increase) up to 50 p.p.m.	General decrease From 25 p.p.m.—improvement General improvement	By low-current-density treatment (2-4 amp./ft.^{2}) down to 1 p.p.m. Cannot be removed by high-pH treatment without much loss of nickel

ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

GENERAL

Electrolytic Polishing of Ferrous Metallographic Specimens

F. W. BOSWELL: 'Electropolishing of Ferrous Metal Specimens for Electron Metallography.'

Proc. Amer. Soc. Testing Materials, 1956, vol. 56, pp. 426–35.

Appendix IV to Report of A.S.T.M. Committee E-4 on Metallography.

Although electrolytic polishing has certain obvious advantages, *vis-à-vis* mechanical polishing, for the preparation of electron-microscope specimens, limitations inherent in the process have impeded its full development. These problems are reviewed by the author, as an introduction to a report on a method of electrolytic polishing which is claimed to minimize and, in some cases overcome, such limitations.

The work described covered a critical examination of all the types of electrolyte which have been recommended for use on ferrous materials, with the exception of those based on perchloric acid, which are considered to be undesirable for general laboratory use.

All except one of the electrolytes examined caused etching of the surfaces, a feature undesirable in electron metallography, but the chromic-acid electrolyte recommended by MORRIS (*Metal Progress*, 1949, vol. 56, p. 696) produced surfaces which were practically unetched. This technique was also free from certain other limitations inherent in some of the other methods which have been recommended: high polish is produced, equipment required is simple, polishing times are reasonably short, surface waviness produced on the specimen is only slight, and the method is applicable to a variety of ferrous alloys, of varying microstructure. The technique recommended by the author is a modification of the Morris method, and this note gives full details of procedure. The electrolyte used contains 133 ml. of glacial acetic acid (99·5% by wt. min.), 25 g. of chromic acid (CrO_3), and 7 ml. of water. The equipment used is illustrated.

The suitability of the method is demonstrated by typical electron micrographs showing pearlite in eutectoid steel, bainite and martensite in eutectoid steel, structures of low-chromium steel transformed under various conditions, and orange-peel structure in high-purity alpha iron.

Vapour Pressures of Metals

R. E. HONIG: 'Vapour Pressure Data for the More Common Elements.'

R.C.A. Rev., 1957, vol. 18, June, pp. 195–204.

Correlation of authentic data available up to March 1, 1957. The compilation is based on values obtained by many investigators, who measured vapour pressures by various techniques, under widely differing experimental conditions. An attempt has been made to correlate as closely as is justifiable among the various results reported. Major use has been made of three earlier summaries of vapour-pressure data, to which appropriate reference is made in the text and ***bibliography***.

The data assembled in the present review relate to vapour pressure, melting points and boiling points, and heats of sublimation, for 57 elements which are considered to be of practical importance, particularly in connexion with electronics and high-vacuum technique.

The values quoted for nickel are shown below:

	°K.	°C.
Melting Point	1725	1452
Boiling Point	3112	2839

Chromatographic Analysis

G. VENTURELLO and A. M. GHE: 'The Use of Elution Chromatography from Cellulose Columns for the Systematic Analysis of Special Steels.'

Analyst, 1957, vol. 82, May, pp. 343–52.

The paper describes a chromatographic method for determination of the following elements in steels: molybdenum, cobalt, manganese, vanadium, nickel and chromium. The procedure involves a micro-chemical colorimetric determination of the elements,

Temperatures for Vapour Pressures of Nickel (mm. Hg)

	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10^{1}	10^{2}
°K.	1185	1260	1330	1415	1520	1630	1770	1940	2150	2400	2750
°C.	912	987	1057	1142	1247	1357	1497	1667	1877	2127	2477

which are fractionally separated by elution from cellulose columns. The method is widely applicable and highly sensitive, making possible the estimation of amounts of the order of 1 μg in the eluate. Its accuracy is demonstrated by typical determinations of the elements named, in standardized steels of various types. The range for which determinations of nickel are given covers 0·26 to 11·90 per cent.

Microchemical Analysis: Reference Data

G. W. C. MILNER and J. W. EDWARDS: 'Microchemical Analysis.'

Metallurgical Reviews, 1957, vol. 2, No. 6, pp. 109–55.

Monograph comprising a correlated summary of available information, supported by a *bibliography* of 205 items.

The first part of the review covers the various techniques used in microanalysis, with a brief survey of their advantages and disadvantages. The subject is treated in the following sections: microvolumetric analysis, microgravimetric analysis, absorptiometry, polarography, electroanalysis, electrometric-titration methods, radiochemical methods, chromatographic methods, ion-exchange methods, microanalysis of gases, and miscellaneous procedures.

The second part is concerned with the applications of the various techniques to specific groups of material: it deals with analysis of steels, aluminium alloys, and copper-, tin-, zinc-, nickel- and magnesium-base alloys. Methods for determination of nickel are included in the steel, aluminium alloys and copper-base alloys sections.

NICKEL

Reduction of Nickel by Hydrogen from Ammoniacal Nickel-Sulphate Solutions

V. N. MACKIW, W. C. LIN and W. KUNDA: 'Reduction of Nickel by Hydrogen from Ammoniacal Nickel-Sulphate Solutions.'

Trans. Amer. Inst. Mining and Metallurgical Engineers, 1957, vol. 209, pp. 786–93; ***T.P.*** 4442D.
Jnl. of Metals, June 1957.

In the process employed by Sherritt Gordon Mines, Ltd., for production of metallic nickel, a sulphide concentrate is leached with ammonia and air, under pressure. Following the removal of iron, copper and other impurities, there remains a purified solution having the following composition (g./L.):

Nickel 40–50; $(NH_4)_2SO_4$, 200–400; NH_3, 20–30.

From this solution metallic nickel is reduced by hydrogen under pressure at 300°–350°F. (148°–176°C.), in mechanically agitated autoclaves.

A catalyst, ferrous sulphate, is required to initiate the first reduction. After the reduction the depleted solution is discharged, leaving the metallic nickel in the autoclave, and the nickel produced, being in a finely divided form, is used as a catalyst for reduction of the next batch of solution. On repeated use the metallic nickel particles increase in size and become more compact, resulting in production of a powder having higher apparent density. Each reduction is therefore termed 'densification'. Finally, when the burden of metal powder in the autoclave becomes too great to permit of effective agitation, both powder and depleted solution are discharged. The autoclave is then filled with fresh solution, ferrous-sulphate catalyst is added, as before, and a new cycle is started. (The cycle of operations has been fully described in earlier papers, to which references are given in the *bibliography*.)

This latest communication in the series relating to the Sherritt Gordon process reports the results of a detailed examination of the reaction by which nickel can be precipitated from aqueous ammoniacal nickel-sulphate solutions by hydrogen, at elevated pressures and temperatures. The thermodynamics of the reactions are discussed and the behaviour of ammonia is illustrated. The authors propose a mechanism to account for the catalytic effect of ferrous-salt additions, and describe the influence of certain variables (hydrogen pressure, temperature, catalyst concentration, etc.) on the autocatalytic nature of the reduction, with particular reference to the dependence of the rate of reaction on the available surface area of nickel metal.

It is suggested that the autocatalysis resulting from the formation of metallic nickel nuclei may be explained by assuming a constant rate of formation of the nuclei and a direct proportionality between the rate of reduction and the number of the nuclei.

It is believed that the nuclei probably not only grow during reduction, but also agglomerate into larger-sized particles and gradually assume the spherical form. When a certain critical size is attained the agglomeration process ceases and the particles grow symmetrically in all directions. At that stage the rate of reduction is found to be directly proportional to the calculated surface area of the nickel particles.

Surface Tension of Liquid Nickel

P. KOZAKEVITCH and G. URBAIN: 'Surface Tension of Pure Liquid Iron, Cobalt and Nickel at 1550°C.'

Jnl. Iron and Steel Inst., 1957, vol. 186, June, pp. 167–73.

The measurements reported were carried out by an improved version of the sessile drop method, described by the authors in 1955 (*Rev. Métallurgie*, vol. 52, pp. 139–60).

Vapour Pressure of Nickel

See abstract on p. 156.

Oxidation of High-Purity Nickel

E. A. GULBRANSEN and K. F. ANDREW: 'High-Temperature Oxidation of High-Purity Nickel between 750° and 1050°C.'

Jnl. Electrochemical Soc., 1957, vol. 104, July, pp. 451–4.

The literature relating to the oxidation of pure

nickel was reviewed in an earlier paper by the present authors (*ibid.*, 1954, vol. 101, pp. 128–40; *Nickel Bulletin*, 1954, vol. 27, No. 5, p. 81). Earlier investigations had covered oxidation at temperatures up to 900°C.: this later report extends the range to 1050°C.

The principal aim of the work was two-fold: (1) comparison of oxidation-rate data with results of tracer studies of the diffusion of nickel ions through nickel oxide, and (2) determination of the conditions in which the mechanism of oxidation changes.

Studies on some other metals have shown that, at some thicknesses of oxide, transition occurs from a slow, protective oxide formation to a more rapid non-protective oxidation. The technical significance of such a change is obvious, since in many high-temperature applications of metals and alloys service life of the materials depends on the ability of the oxide to limit the rate of oxidation. Within the 'protective' oxide-formation range the rate of oxidation slows down as the oxide film thickens, but at some temperature, time, and oxygen pressure, or film-thickness, the rate of oxidation undergoes a transition to a more rapid reaction, in which the rate of reaction does not depend on the thickness of the oxide coating on the metal. This phenomenon has been variously described as 'catastrophic reaction', 'catastrophic oxidation', 'breakaway corrosion', 'transition reaction', etc., depending on the degree of change in the reaction kinetics. In the present paper the alteration is referred to as 'failure in protective oxidation'.

The following physical and chemical factors have been related to the onset of transition in the kinetics of the reaction: (*a*) volatilization of the oxide; (*b*) volatilization of the metal; (*c*) phase transformations in the oxide; (*d*) phase transformations in the metal; (*e*) melting of the oxide; (*f*) loss of adhesion of the oxide to the metal; (*g*) combustion.

From experimental observations made on (1) the colour of the oxide film (determined by the conditions in which it is formed), (2) the cracking of the oxides on cooling, and (3) the deviations from the parabolic law, it is concluded that at temperatures at which nickel oxide fails to give protective oxidation the failure is due to a localized loss of adhesion at the interface between the oxide and the metal. For the grade of nickel studied (which had no metallic impurities in excess of 0·0005 per cent.) protective oxidation fails at about 900°C., at which temperature the parabolic rate law constant has a value of $1{\cdot}88 \times 10^{-11}$ $(g/cm^2)^2/sec.$ and a film-thickness value of 400–600 $\mu g/cm^2$.

The failure of the oxide-metal adhesion may be related to one of several factors:

(*a*) Stress may exist at the interface, due to a mismatching of the nickel and nickel-oxide lattices, leading to failure as the oxide grows to a thick film.

(*b*) Oxygen may dissolve in the nickel, a process which could lead to small changes in the physical and chemical properties of the oxide-metal interface, with possible ultimate failure.

(*c*) Since oxidation results from a diffusion of nickel through the oxide, the oxide must continuously collapse onto the metal as nickel diffuses from the oxide-metal interface. This process will not occur uniformly, due to the different reaction rates on the several crystal orientations of the metal grains. Thus, cohesion between the oxide crystals and cohesion between the alloy and oxide would be diminished.

Nickel Anodes: Specification

See abstract on p. 160.

Sintered-Plate Nickel-Alkaline Batteries

G. W. WORK: 'A Sintered-Plate Nickel-Cadmium Cell.'

U.S. Naval Research Laby., N.R.L. Report 4852, Oct. 30, 1956; 13 pp.
P.B. 121533.

Report on examination of a specimen cell of a type now in commercial production in the U.S.A. An evaluation of over 700 cycles, under varied conditions of temperature, charge and discharge rates, and stand, indicates that this type of cell will give satisfactory performance at temperatures at least as low as 0°F. (−18°C.), that it is capable of being fully charged in less than one hour, and that it can be discharged in a few minutes without excessive loss of capacity. Capacity loss during a 90-day stand is of the order of 20–25 per cent. at room temperature, and considerably less at 0°F. (−18°C.). After 700 cycles the capacity was still 20 per cent. above the rated value: there was thus no indication of the approach of the end of cycle life. The cell appeared to be rugged, both physically and electrically.

Determination of Aluminium in Cathode Nickel

G. ECKERT: 'Analysis of Nickel Alloys for the Manufacture of Cathodes. III. The Determination of Aluminium.'

Zeitsch. f. analytische Chemie, 1956, vol. 153, pp. 261-7.
Analytical Abstracts, 1957, vol. 4, No. 4, Abs. 1230.

'The colorimetric determination of small concentrations of aluminium (0·01–0·002 per cent.) in nickel alloys, by means of aluminon, is described. Aluminium is freed from the large excess of nickel and other metals such as cobalt, iron, manganese, vanadium, lead, tin and copper, by extracting these metals with sodium diethyldithiocarbamate in a non-polar chlorinated hydrocarbon solvent (CCl_4, dichloroethylene). Silicon and magnesium do not interfere, but tungsten, titanium and chromium must be substantially removed before the final colorimetric determination of aluminium with aluminon. The method is suitable also for determining aluminium in iron alloys.'

Determination of Silicon in Nickel and Nickel Alloys

T. R. ANDREW: 'The Photometric Determination of Small Amounts of Silicon in Nickel and Nickel Alloys used in Electronic Devices.'

Analyst, 1957, vol. 82, June, pp. 423–7.

Although numerous variants of the molybdenum-blue method have been proposed for the determination of silicon in nickel, none of the procedures suggested has proved suitable for examination of material containing less than 0·01 per cent. of silicon. This paper describes work done in the laboratories of The Mullard Valve Company, on a modified version of the ferrous-sulphate/oxalic-acid procedure recently described by ANDREW and GENTRY as applied to estimation of silicon in steels (*ibid.*, 1956, vol. 81, p. 339). The tests reported were specifically designed to evaluate the suitability of the modified method for determination of low concentrations of silicon in nickel.

Since nickel for cathodes often contains additions of tungsten, experiments were made with alloys containing up to 4 per cent. of tungsten. It was anticipated that difficulty might be caused by the presence of that element, which is precipitated under the conditions used, and although it has been claimed that no silicon is lost in the precipitate, it was considered preferable, in view of the small amounts of silicon involved, to have complete solution of the tungsten. The use of oxalic, tartaric or citric acid to hold the tungsten in solution was not possible, since these acids prevent formation of molybdosilicate, and although with the hydrofluoric-acid solution technique recommended by Case the tungsten-containing alloys were completely dissolved, a precipitate of tungstic acid formed when the fluoride was complexed with boric acid. It was found, however, that within certain limits phosphoric acid could be used to give a clear solution in which silicon could be photometrically determined.

Silicon is photometrically determined at 810μ, as the blue reduced molybdosilicate. A precision of $\pm$0·001 per cent. of silicon is claimed, on a sample weighing 0·25 g., and the method can be used on samples weighing only 12·5 mg., such as may be available as single cathodes from electronic valves.

The use of phosphoric acid to retain tungsten in solution restricts the acidity range within which quantitative formation of molybdosilicate is achieved, but the permissible tolerance of acid concentration is sufficiently great to permit the method to be used for routine determinations.

Determination of Nickel in Reduced Oxide

F. J. SCHMIDT: 'High-Frequency Determination of Ferromagnetic Metals.'

Analytical Chemistry, 1957, vol. 29, July, pp. 1060–2.

In the metals industries reduction of oxides to metals is a common practice. Many process variables must be closely controlled in order to obtain products within specified limits of reduced-metal content and, for greatest economy and usefulness, the routine analytical control methods should be simple and rapid. This paper describes a procedure in which it is possible to employ relatively large and coarse laboratory samples, which can be prepared more quickly than the smaller and more elaborately treated specimens usually necessary. The new method is based on magnetic-permeability measurements at high frequencies, the results being calibrated in an empirical manner by means of chemically analysed samples. The procedure is suitable for determination of iron, nickel or cobalt when only one of these metals is present as a major constituent. Apparatus and technique are fully described, with drawing, and results obtained on reduced nickel-oxide samples are discussed in detail.

Microchemical Analysis: Reference Data

See abstract on p. 157.

Chromatographic Analysis

See abstract on p. 156.

Welding of Nickel

See abstract on p. 163.

Standard Samples of Nickel Oxide

'Standard Samples of Nickel Oxide.'

Nat. Bur. Standards, Tech. News Bull., 1957, vol. 41, No. 2, p. 23.

Two new standard samples of nickel-oxide powder, of which the compositions are shown below, are the averaged analytical results of tests by fourteen co-operating laboratories representing the National Bureau of Standards and producers and consumers of nickel.

The standards may be used in checking and calibrating both spectrochemical and chemical methods employed in the analysis of nickel, particularly metal of cathode grade.

N.B.S. No.	Co %	Cu %	Fe %	Mg %	Mn %	Si %	Ti %	Al %	Cr %
671	0·31	0·20	0·39	0·030	0·13	0·047	0·024	0·009	0·025
672	0·55	0·018	0·079	0·020	0·095	0·11	0·009	0·004	0·003

Physical Properties of Nickelous Oxide at Sub-Zero Temperatures

E. G. KING: 'Heat Capacities at Low Temperatures and Entropies at 298·15°K. of Nickelous Oxide, Cobaltous Oxide and Cobalt Spinel.'

Jnl. Amer. Chemical Soc., 1957, vol. 79, May 20, pp. 2399–400.

This paper presents heat-capacity measurements in the temperature range 50° to 298°K. (−223° to +25°C.), and entropy values at 298°K., for crystalline nickelous oxide (NiO), cobaltous oxide (CoO) and cobalt spinel (Co_3O_4). Details are given of the preparation of the materials from which the data were determined: the heat-capacity calorimeter used was described earlier (*U.S. Bur. Mines Tech. Paper* 686, 1946).

The temperature/heat-capacity curves of nickelous oxide and cobalt spinel show irregular behaviour within the limits studied. The values for heat-capacity of nickelous oxide are in general lower than those measured by Seltz *et al.*: the discrepancies vary at different temperatures.

Entropies at 298·15°K. were calculated by various methods, details of which are given: the findings are summarized as follows:

Nickelous oxide ..	9·08±0·04	cal./deg. mole
Cobaltous oxide ..	12·66±0·08	,, ,,
Cobalt spinel ..	24·5 ±0·2	,, ,,

Nitriding of Nickel

J. J. TRILLAT, L. TERTIAN, N. TERAO and C. LECOMTE: 'The Action of Nitrogen on Nickel.'

Bull. Soc. Chimique de France, 1957, June, pp. 804–9.

This is the full account of experiments referred to in the communication published in *Comptes Rendus de l'Académie des Sciences*, 1957, vol. 244, pp. 596–8: see *Nickel Bulletin*, 1957, vol. 30, No. 6, p. 85.

Determination of Nitrate and Chloride in Sodium-Hydroxide Solution

G. GABRIELSON and B. ANDERSSON: 'The Determination of Nitrate and Chloride in Sodium Hydroxide Solution by Means of Cation Exchanges in the Manufacturing Control of Alkaline Batteries.'

Analytica Chimica Acta, 1957, vol. 16, May, pp. 425–7.

The authors classify the main types of alkaline battery and describe preparation of the positive and negative plates of the sintered-plate nickel-cadmium cell. These consist of highly porous structures of nickel impregnated, respectively, with nickel hydroxide and cadmium hydroxide which, during charging, form, in the one case higher nickel oxides, and in the other cadmium metal. After impregnating, the plates are immersed in strong sodium hydroxide and the corresponding hydroxides precipitate in the pores. The plates are then rinsed in water and dried at 80°C. This cycle is repeated three or four times, after which the plates are ready for charging.

The sintered nickel plates, the porosity of which is about 80 per cent., absorb a large volume of the impregnating salt solution, which results in the rapid neutralization of the sodium hydroxide, and the necessity for adding a further amount. The nitrate and chloride concentrations in the hydroxide solutions are thus increased and, since these ions are injurious to the alkaline battery, it is important to ensure that they are not present in too high a concentration. As a control method, an accurate procedure has been developed by which these ions can be determined in the sodium-hydroxide solution.

The solution is passed through a cation exchanger in the hydrogen form and the effluent is titrated with 0·1*N* sodium hydroxide, in the presence of methyl orange as indicator. Details are given of apparatus and procedure.

ELECTRODEPOSITION AND OTHER COATING METHODS

Nickel Anodes: Specification

COMMISSIONER, FEDERAL SUPPLY SERVICE, GENERAL SERVICES ADMINISTRATION, U.S.A.: 'Federal Specification for Nickel Anodes.'

Specification QQ-A-677, Mar. 22, 1957: superseding *Specification* QQ-N-265 of Aug. 17, 1944.

The specification governs supply of two types of nickel anode designated, respectively, carbon type, and oxide type.

Type 1 (which is usually cast) is intended especially for use in plating solutions having a pH of 4 or below. It is the grade preferred for use in bright plating baths.

Type 2, depolarized anodes, are usually rolled nickel, and are primarily intended for use in solutions of pH above 4.

The chemical composition limits laid down for the two types are shown below.

Sampling and test procedures are included in the specification, which also contains (for guidance only) full details of methods of chemical analysis suitable for use on anode nickel.

	Ni+Co %	Fe %	Cu %	S %	Si %
Type 1	99·00 min.	0·15 max.	0·08 max.	0·02 max.	0·20—0·35
Type 2	99·00 ,,	0·15 ,,	0·10 ,,	0·01 ,,	0·02 max.

Effects of Impurities in Nickel-Plating Solutions

A. J. SMITH: 'The Effect of Impurities in Nickel-Plating Solutions.'

Plating, 1957, vol. 44, May, pp. 500–1.

In connexion with the 1957 Annual Meeting of the American Electroplaters' Society summary reports were prepared to show the work completed by the various Research Project Committees of the Society. Among these reviews was one relating to the influence of impurities in various types of nickel-plating solution, a research which has covered the effects of nine contaminants. In each case a study has been made of the influence of the impurities on the appearance of the deposits, their ductility, hardness, and (salt-spray) corrosion-resistance. The effect of impurities on the throwing power of the solutions, and methods for removal of contaminating media, have also been investigated. The individual reports have been abstracted in *The Nickel Bulletin* at the times of issue, and a detailed summary, based on the findings of the A.E.S. research, has now been prepared in the form of a reference table, which appears on pp. 152–155 of this Bulletin.

Determination of Impurities in Plating Solutions

E. J. SERFASS: 'Determination of Impurities in Plating Solutions: Major Constituents: Cyanides in Plating Wastes.'

Plating, 1957, vol. 44, May, pp. 504–5.

Summary of work completed under A.E.S. Research Project 2. Reference is given to 39 individual reports published over the period 1945–1956. Those relevant to electrodeposition of nickel have been abstracted in *The Nickel Bulletin* as published.

Physical Properties of Electrodeposited Nickel

A. BRENNER: 'Physical Properties of Electrodeposited Metals: Nickel.'

Plating, 1957, vol. 44, May, pp. 497–8.

Summary of work completed under Research Project 9 sponsored by the American Electroplaters' Society. Comprehensive work, done over a long period, has led to the following conclusions:

The most important factor determining the properties of electrodeposited nickel is the type of solution used. Within the normal limits, operating conditions have only relatively small effects.

A chart accompanying this summary report shows the following properties, as influenced by the nature of the solutions from which the deposits are made: stress in the deposit, hardness, tensile strength, elongation, resistivity, coercive force, maximum permeability. The properties are related to deposits made from five main types of solution: (1) bright-nickel, (2) high-chloride, (3) baths containing sulphates and chlorides in equal proportions, (4) chloride-free sulphate, and (5) Watts-type. The general trends revealed by the values shown are noted below:

'The Watts-type deposits have the lowest stress, hardness, tensile strength, resistivity, and coercive force and the highest elongation and magnetic permeability. Bright-nickel deposits have the highest hardness, tensile strength, resistivity and coercive force, and the smallest elongation and magnetic permeability. Most other nickel deposits can be assigned to one of these main groups. Thus, the deposits from the fluoborate bath belong to the Watts-type group, whereas the deposits from ammoniacal baths approach bright-nickel deposits in properties, especially with regard to hardness, tensile strength and resistivity.

'The properties of an electrodeposit are determined primarily by the chemical and physical nature of co-deposited impurities. The parallel trend of many of the properties shows that a common cause underlies their variations. Correlations have been shown to exist between the properties and the microstructure and X-ray structure of the deposits. Since the largest changes in structure and in properties result from variations in the nature of the plating solution, particularly in the presence of certain types of ions or minute amounts of special additions, it is reasonable to assume that the special character of the deposits is caused by the co-deposition of various kinds of foreign matter which may vary in quantity as well as in effectiveness.

'The general tenor of the discussion is that the electrodeposited coatings that are of value in industry are not pure metals, but owe their valuable properties to the presence of small amounts of co-deposited impurities.

'The mechanism by which foreign material is co-deposited is a matter of speculation, but it is likely that it is an adsorption phenomenon rather than an electrochemical one, as has sometimes been postulated. The adsorption mechanism is sufficiently broad and versatile to explain the very specific effects of certain additives to the plating solution and the influence of the anion of a plating solution on the nature of the deposit. Future research should be directed towards the study of these adsorption phenomena and the processes taking place in the cathode film during electrolysis. More delicate methods of analysis for the small amount of impurities usually present are needed, in order to correlate the content of foreign material with lattice distortion and crystal structure, believed to be the basis for the observed large differences in physical and mechanical properties of nickel electrodeposits.'

Nickel Plating of Cast Iron

E. ALARY: 'Bright Nickel Plating on Cast Iron: Development of a Production Process.'

Electroplating and Metal Finishing, 1957, vol. 10, July, pp. 227–8.

The article deals with problems involved in plating domestic irons, various parts of which, including the cast-iron sole plates, were to be coated with bright nickel and finished with chromium. Two main difficulties were encountered: (1) defects arising from the structure of the sole plate, and (2) the development of a 'frosted' surface on the nickel on cooling from the temperature at which the irons were used (about 350°C.).

Full details are given of the sequence of cleaning and plating operations developed (which is now being used for treating some 1000 irons per day). The degreasing and cleaning media recommended are proprietary brands, and the nickel-plating bath used is the Efco–Udylite type 31H. An alkaline copper undercoat is used and the final coating of chromium is applied in such a manner as to ensure elimination of the frosting of the nickel, which had been found to be caused by the use of a very high current density during deposition of the chromium.

Electroless Deposition of Nickel: Kanigen Plating

'Official Approval for Kanigen Plate.'

Sheet Metal Industries, 1957, vol. 34, July, p. 502.

The Kanigen plating process, which is now being operated on a production scale in the United Kingdom, Eire and Denmark by Messrs. Albright and Wilson (Mfg.), Ltd., has recently been given the Ministry of Supply designation D.T.D. 900/405. The Ministry has indicated approval of the use of the process for plating of certain carbon and low-alloy steels, stainless steels, and aluminium. Similar approval has been given by the Air Registration Board, under the reference number AI/5112/57. A range of articles has already been plated by the new process and co-operative work is in hand between platers and design engineers with a view to extending its application to other items for which the properties of Kanigen plate appear specially suitable.

Electronic Measurement of Thickness of Electrodeposited Coatings

F. P. BRODELL and A. BRENNER: 'Further Studies of an Electronic Thickness Gauge: Circuitry, Operating Characteristics and Calibration.'

Plating, 1957, vol. 44, June, pp. 591–601.

This report is a sequel to a paper published in the same journal in 1953 (vol. 40, p. 1238), which described an electronic thickness gauge utilizing the principle of the skin effect, to measure thickness of metallic coatings on a metal base. This later report describes results obtained in a further study of the gauge, made with a view to testing its general utility for routine operation.

The 'skin effect', upon which the operation of the gauge depends, is the tendency of alternating currents to travel closer and closer to the surface as the frequency is increased. With other parameters fixed, the strength of the current depends on the conductivity of the surface layers. The thickness gauge utilizes a small probe coil energized with an alternating current of radio frequency, to induce an eddy current in a plated metallic surface. The frequency of the current is so chosen that, by virtue of the skin effect, an appreciable proportion of the eddy current flows in both the basis metal and the coating. Provided that the coating and basis metal have different electrical conductivities and/or magnetic properties, the strength of the induced eddy current varies with the thickness of the coating. The strength of the induced current is indirectly measured through the interaction of its magnetic field with the probe coil, and the net result is a change in the apparent impedance of the probe coil. The current through the probe coil changes correspondingly, and the amount of the change, or the unbalance of a circuit, is measured with a microammeter.

The thickness of a coating is thus translated into a change in the reading on the microammeter, and, by calibrating the gauge with standard coatings of known thickness, the meter readings are directly related to the thickness of the coatings. (The gauge has been named the 'Dermitron', from the neo-Latin word *dermis*, derived from the Greek word *dermos*, skin.)

Several improvements which have been incorporated in the latest design of the instrument are described, and results are given of calibrations of the gauge for several combinations of coatings and basis metals. The observations made have indicated that (1) calibrations of different gauges are similar, (2) the method is unsatisfactory for determinations of thickness of nickel coatings, except under very restricted conditions, and (3) measurement on poorly conductive and non-conductive coatings require a technique differing slightly from that suitable for evaluation of highly conductive coatings.

Nickel in Cast Irons for Enamelling

See abstract on p. 166.

NON-FERROUS ALLOYS

Ageing of Copper-Nickel-Manganese Alloys

T. TAKEUCHI: 'Ageing of Copper-Nickel-Manganese Alloys.'

Report, Govt. Industrial Research Inst., Nagoya, 1956, vol. 5, No. 11, pp. 537–43.

Copper-nickel-manganese alloys containing 10–70 per cent. nickel + manganese, in equal parts by weight, were tested for hardness, shear modulus, electrical resistivity and crystal structure, after being held at temperatures of 250°–550°C. for times ranging from one minute to several hundred hours. The observations made are summarized in *Metallurgical Abstracts*, 1957, vol. 24, June, p. 797.

Structural Examination of Precipitation-Hardening Nickel-Chromium Alloys

See abstract on p. 168.

Forming Qualities of Nickel Silver

J. T. RICHARDS and E. M. SMITH: 'Factors Affecting the Forming Properties of Several Copper Alloys in Strip Form.'

Proc. Amer. Soc. Testing Materials, 1956, vol. 56, pp. 807–22.

This paper reports a section of a comprehensive

investigation which is being carried out to evaluate the forming characteristics of spring materials. Bend-, tension- and hardness-test results are presented for beryllium-copper, phosphor-bronze, 70-30 brass, gilding metal (95-5 copper-zinc), and two grades of nickel silver (12 and 18 per cent. nickel). The influence of temper, thickness of strip, direction of grain and grain size was studied for each material. Formability was rated in terms of the minimum safe radius for cold-forming a 90° bend.

The test results are reported in extensive tables and graphs, from which the following general conclusions are drawn:

'The softer tempers can be bent sharp to a 90° angle without cracking or displaying 'orange peel'. Harder tempers require increasing radii for safe bending.

'Most of the materials tested displayed directionality in bend and tension tests, particularly when tested in the harder tempers. Strip having relatively fine grain-structure offers the best combination of formability and tensile properties. For a given level of formability, beryllium-copper showed the highest strength and hardness, and it is noted that nickel silver also gives, at any selected formability level, better strength than is obtained in phosphor bronze or brass.'

Electrical Resistivity of Nickel-Palladium Alloys

A. W. OVERHAUSER and A. I. SCHINDLER: 'Electrical Resistivity of Nickel-Palladium Alloys.'

Jnl. Applied Physics, 1957, vol. 28, May, pp. 544-6.

It was anticipated that the concentration dependence of residual resistivity in nickel-palladium alloys would obey a simple Nordheim law, since the number of holes in the *d* band and the number of electrons in the *s* band are approximately independent of composition. Measurements have indicated, however, that maximum resistivity occurs at 70 at. per cent. palladium, not at 50 per cent. The authors advance an explanation for this behaviour.

Welding of Nickel and High-Nickel Alloys

J. HINDE: 'The Joining of Nickel and High-Nickel Alloys.'

Engineer and Foundryman, 1957, vol. 22, May, pp. 52-63; disc., pp. 63-4.

Reprint of paper presented to the South African Institution of Welding, January 1957.

The paper contains a comprehensive general survey of technique which may be used in the welding of nickel and of high-nickel alloys of the nickel-copper-, nickel-molybdenum- and nickel-chromium-(iron)-base types.

It is noted that these materials may be welded by all the usual methods (except submerged-arc welding, for which no appropriate fluxes or filler metals are yet available), and that in many respects the techniques suitable are closely similar to those used for welding steel. Certain variations in practice are, however, necessary. The author therefore concentrated on details of welding practice essential in the joining of nickel and its alloys, giving information on the physical properties of the materials which influence their welding characteristics, the composition limits of the respective types, the types of electrode and filler materials which may be used, methods of preparation for welding, welding operations, post-weld treatment, and finishing. Factors affecting the choice of the welding process used for specific applications are discussed, followed by consideration of conditions suitable for joining the high-nickel materials by oxy-acetylene, argon-arc, metallic-arc and resistance welding. Brief reference was also made to other welding processes which, though less generally used, may have useful application in certain cases, e.g., atomic-hydrogen welding and flash welding. Throughout the paper emphasis is laid on the necessity for adequate cleaning before welding, in order to prevent contamination by dirt, oil, grease, drawing compounds, paints, oxide films, etc. Other aspects to which reference was made included the properties of welded joints in relation to individual applications, and the influence of surface finish on corrosion-resistance.

Some consideration was given to soldering and brazing, with particular reference to silver-soldering and to some high-temperature brazing alloys which have recently been developed. Attention was also directed to two important applications of high-nickel alloys which are closely akin to welding, *viz.*, surfacing with nickel-chromium alloys of the Brightray type or with nickel-chromium-boron alloys, and the use of clad materials, for which special welding techniques have been developed.

Copper-Nickel Heat-Exchanger Tubes

BRIT. STANDARDS INSTN.: 'Solid-Drawn Copper-Alloy Tubes for Heat-Exchange Equipment in the Petroleum Industry.'

B.S. 1464: 1957; 24 pp. Price 4/-.

This specification is a revision of a schedule issued in 1948 as one of a series of standards for equipment in the petroleum industry. In the earlier version the specification applied only to aluminium-brass and Admiralty-mixture brass tubes, but the second edition has been extended to cover heat-treated solid-drawn tubes of 7 per cent. aluminium bronze, 70-30 arsenical brass and 70-30 copper-nickel. The specification gives detailed requirements with regard to dimensional tolerances and mechanical properties, and lays down conditions for hardness, drift and flattening tests, and for determination of susceptibility to stress-corrosion cracking, by means of the mercurous-nitrate test. An appendix contains photomicrographs illustrating grain-size standards for the respective alloys.

Composition limits for the 70-30 copper-nickel alloy are as follows: nickel 30·0-32·0: iron 0·40-1·00: manganese 0·50-1·50, per cent., copper remainder.

Nickel-containing Alloys for Brazing Zircaloy

See abstract on p. 176.

Determination of Aluminium in Cathode Nickel Alloys

See abstract on p. 158.

Determination of Silicon in Nickel Alloys

See abstract on p. 159.

Microchemical Analysis: Reference Data

See abstract on p. 157.

NICKEL-IRON ALLOYS

Anhysteretic Magnetization in Nickel-containing Magnet Alloys

E. P. WOHLFARTH: 'The Anhysteretic Magnetization of Permanent-Magnet Alloys.'
Philosophical Magazine, 1957, 8th Ser., vol. 2, June, pp. 719–25.

Calculations, on the basis of the single-domain treatment, are reported for the anhysteretic magnetization, the anhysteretic remanent magnetization and the initial magnetization, for a simple model of a permanent-magnet alloy, and the results are compared with experimental curves for Alcomax III.

Nickel-Iron Laminations for Transformers and Chokes

BRIT. STANDARDS INSTN.: 'Nickel-Iron Transformer and Choke Laminations.'
B.S. 2857: 1957; 11 pp. Price 3/–.

This specification covers non-oriented nickel-iron laminations, insulated or uninsulated, made from materials designated as follows:

Class A. Approximately 76 per cent. nickel, plus additions, the bulk of which is iron.

Class B. Approximately 50 per cent. nickel, 50 per cent. iron.

Class C. Approximately 36 per cent. nickel, plus additions, the bulk of which is iron.

Class D. Approximately 36 per cent. nickel, 64 per cent. iron.

The requirements laid down in Section 1 include thickness tolerances, burr limits, surface finish, space factor and minimum permeability.

Section 2 deals with audio-frequency tests on lacquered nickel-iron laminations.

Appendix A gives details of the method of testing to be used for the determination of space factor, and Appendix B describes a method of determining the permeability of laminations when testing for compliance with the guaranteed minimum permeability values called for in the specification.

Oxidation of Nickel-Iron Alloys

R. T. FOLEY, C. J. GUARE and H. R. SCHMIDT: 'Oxidation of Iron-Nickel Alloys. II. Electron Diffraction at High Temperatures.'
Jnl. Electrochemical Soc., 1957, vol. 104, July, pp. 413–17.

The authors draw attention to the many industries in which nickel-iron alloys now play an important part, and point out that the oxidation characteristics of such materials are therefore of considerable interest. Examination, by the electron-diffraction technique, of the films formed is of particular value in the study of oxidation, because the electron beam penetrates only to a depth of less than 50Å.

It has been previously indicated that the most useful information is obtained when measurement is made at the temperature of the actual oxidation reaction, thus avoiding the transformations and decompositions which take place on cooling, and may vitiate the interpretation of the reaction mechanism. This paper describes observations made on three alloys, at 600°, 700°, 800° and 900°C. The special high-temperature electron-diffraction furnace employed is described and illustrated.

The alloys used were binary types containing, respectively, 30 and 41 per cent. of nickel, and a ternary alloy containing nickel 78, molybdenum 3·8, per cent., balance iron. The results indicate that at the elevated temperatures of test more than one oxide was present on the alloys. Contrary to conclusions drawn from exclusively room-temperature tests, the oxide predominant on the 30 and 41 per cent. nickel alloys was the ferrite (Fe_3O_4 or $NiFe_2O_4$) rather than alpha-Fe_2O_3. In the ternary alloy the molybdenum entered into the reaction: at 700° and 800°C. both NiO and MoO_3 were present on the 78 per cent. nickel alloy. The authors comment that, in the light of current theory, the presence of MoO_3 at a temperature above its melting point (795°C.), and one at which it exerts considerable vapour pressure, is difficult to explain.

It was found that in some cases the lattice spacings of the alloy structure were carried over into the first-formed film of oxide. With subsequent growth the spacings achieve the normal (X-ray) values for the oxide.

CAST IRON

Types of Cast Iron and Their Applications

J. G. PEARCE: 'Principal Types of Cast Iron and Broad Spheres of Application.'
Brit. Cast Iron Research Assocn., Jnl. Research and Development, 1957, vol. 6, No. 11, Apr., pp. 521–7; disc., pp. 528–9. *Research Report* 457.

Paper presented to Conference on Engineering Properties and Uses of Iron Castings, London, November 1956.

The author reviewed the principal types of flake-graphite cast iron, nodular iron and special cast irons which are now available to the engineer and

designer. This classification is considered in relation to mechanical requirements laid down in British Standard specifications. The reference to applications is in only general terms.

Production of Alloy Cast Irons and S.G. Iron

W. M. LORD: 'Production Problems in the Manufacture of Alloy-Iron Castings.'

Brit. Foundryman, 1957, vol. 50, May, pp. 258–67.

The paper describes some improvements in production methods which have been made, within the existing buildings of a small foundry, to increase output and to provide a wide variety of alloy-iron and other high-duty castings. The regular production now amounts to some 40 tons per week of castings representing nine different compositions, including Ni-Hard abrasion-resisting cast iron, Ni-Resist heat- and corrosion-resisting types, martensitic and acicular nickel-alloyed irons, and S.G. iron.

Among the highlights which are described are modifications made in the melting plant, the use of oxygen in the air blast, methods of mould preparation and a special form of moulding box, the knock-out and returned-sand system, and core-making methods. In connexion with S.G. iron production, some account is given of experience with the pressure-ladle process. S.G. iron is made also by the original nickel-magnesium process and by plunging of No. 55 (calcium-magnesium-silicon-iron) alloy. The paper includes illustrations of castings made in various nickel-alloy cast irons and in S.G. iron.

Elevated-Temperature Properties of Cast Irons

J. R. KATTUS: 'Properties of Cast Iron at Elevated Temperatures.'

Foundry, 1957, vol. 85, June, pp. 172–4, 176.

The A.S.T.M./A.S.M.E. Joint Committee on Effects of Temperature on Properties of Metals is sponsoring (at the Southern Research Institute, Birmingham, Alabama) an investigation of the elevated-temperature properties of cast irons of plain, alloyed and nodular types. Work to date has covered a literature search; screening tests on twelve commercial cast irons; creep-rupture tests at 800° and 1000°F. (425° and 540°C.) for times up to 5,000 hours, on seven of the most promising materials, and thermal-shock tests on the same irons. The seven types screened for close study are shown in the table at the end of the abstract. The test results to date indicate that the irons are suitable for load-carrying applications at temperatures up to 800°F. (425°C.), in which conditions there was no sharp fall in properties in exposure times of nearly 5,000 hours. The creep-rupture properties of the irons are not, however, promising for applications requiring the support of appreciable loads for long periods at 1000°F. (540°C.).

Alloying has a marked effect on creep-rupture properties: molybdenum has the most potent influence; the chromium-molybdenum-alloyed iron showed the best high-temperature properties of all the irons tested, and the iron alloyed with chromium, nickel, molybdenum and vanadium showed almost equally good properties. Chromium used alone is *not* beneficial with regard to creep-rupture properties. Unalloyed ferritic S.G. iron was slightly superior to unalloyed pearlitic grey cast iron.

The results have not made possible any consistent correlation between the creep-rupture properties of cast iron and its metallographic structure and heat-treatment.

In view of the practical importance of thermal-shock resistance, tests have been made to determine this property at 800°F. (425°C.), the level representing the maximum useful service temperature of cast iron under load. Preliminary study of a number of thermal-test techniques resulted in selection of a method in which the specimen could be cycled while subjected to any desired external bending load. The tube-like specimen formed the centre section of a simple beam which was dead-weight loaded equally at both ends and supported at two points on opposite sides of the specimen.

In carrying out a test, the specimen was loaded and thermally cycled between 800° and 150°F. (425° and 65°C.), and the number of cycles to rupture was determined. The heating time in each thermal cycle was 85 seconds. Cooling was accomplished in 15 seconds by pouring water over the specimens. Both smooth and notched specimens were tested: the notched test was adopted as standard, since it was more severe, and applicable to all materials.

Each iron was tested at various levels of stress, and the results were plotted in the form of thermal-fatigue curves showing stress *vs.* number of cycles to failure.

The resulting data gave the following *descending* order of merit for the respective types in the thermal-fatigue tests:

(1) Unalloyed ferritic nodular iron.
(2) Nickel-molybdenum grey cast iron.
(3) Chromium-molybdenum grey cast iron.
(4) Chromium-nickel-molybdenum-vanadium grey cast iron.
(5) Molybdenum grey cast iron.
(6) Chromium grey cast iron, Unalloyed grey cast iron } Similar results.

S.G. Iron in Marine Applications

A. G. ARNOLD: 'Development and Uses of Spheroidal-Graphite (Nodular) Cast Iron for Marine Applications, with Special Reference to Diesel Engines.'

Brit. Cast Iron Research Assocn., Jnl. Research and Development, 1957, vol. 6, Apr., pp. 588–98; disc., pp. 598–9.

Paper presented to Conference on Engineering Properties and Uses of Iron Castings, London, November, 1956.

One of the most striking trends in the marine field during recent years has been the increasing ascendance of the large slow-running Diesel engine over the geared steam turbine, as a means of propulsion in

the medium-power range. Although the basic reason for this preference is the lower fuel consumption of the Diesel, and its proved reliability even when burning fuels of low grade, it is significant also that the Diesel is still constructed mainly from cast iron and mild steel, whereas the turbine requires the use of more complex and costly materials.

The continuous improvement of the Diesel engine has resulted in more arduous working conditions for the materials from which it is built, and they must therefore be of higher quality, capable of meeting more stringent specifications. The advent of S.G. iron, which is a relatively simple material, having properties intermediate between those of cast iron and of steel, has obviously been of great interest to the marine engineer.

This paper reports experience in the use of S.G. iron in pistons, Diesel-engine liners, and ships' side valves. Problems encountered in such developments are discussed in considerable detail, with particular reference to pistons. Properties required in *piston materials* are considered and, on this basis, high-duty cast iron, S.G. iron and 13 per cent. chromium steel are evaluated. The nature of the failure to which pistons are liable is discussed, and an account is given of improvements which have led to the adoption of S.G. iron as standard for the pistons of 550-mm. and 620-mm. engines. It is hoped that by further modification in composition and heat-treatment of S.G. iron, and by slight alteration in design to reduce the piston temperature, it will later be possible to adopt that material for the pistons of larger Diesel engines.

S.G. iron has also proved satisfactory for one-piece *cylinder liners*, an application in which the introduction of the new material has effected a considerable economy.

For *ships' side valves*, S.G. iron offers a possible alternative to gunmetal and cast steel. Considerable numbers of such valves have been fitted to ships, but trial periods have not yet been sufficiently long to permit exhaustive reports on service life. It is, however, significant that the material continues to be used for this purpose by operators who have already had experience with it. Test criteria applicable to castings for marine service are discussed in this paper.

Diesel-engine bedplates are mentioned as another possible application for S.G. iron: for this application a notch-tough ferritic grade of the iron would be essential.

The authors (who are members of one of the large shipping Companies in the U.K.) conclude that 'it is evident that the uses of S.G. iron in the marine field will multiply as experience of it increases. Eventually it must become one of the materials generally used and accepted by the marine engineer.'

Welding of S.G. Iron and Grey Cast Iron

R. D. WASSERMAN, J. F. QUAAS and J. P. BRODERICK: 'Aspects of Crack Sensitivity in Machinable Deposits on Cast Iron.'

Welding Jnl., 1957, vol. 36, May, pp. 481–8.

The paper reports tests made to evaluate nickel-iron electrodes for welding cast iron. For this work the authors used the test block recommended by SCHUMBACKER and SCHAEFFLER (*ibid.*, 1956, vol. 35, pp. 91S–5S). The block is so designed that welding stresses are not dissipated, and it therefore provides a drastic method of checking the crack-sensitivity of the weld deposit.

The test welds were made by the metallic-arc process and the electrodes used were nickel, nickel-copper and nickel-iron. The various types are described, and some indication is given of the coatings used, which consisted essentially of alkaline-earth carbonates and fluorides, graphite, ferroalloy additions and suitable binders. (The fluorides provide fluxing action and assist in formation of protective slag; the carbonates help in slag formation, provide a gaseous shield, and tend to stabilize the welding arc; the graphite contributes to arc stability and reduces the current necessary for satisfactory welding.) As the basis for the nickel-iron electrode core wire, a 60–40 composition was used, but it is of interest to note the extent to which this ratio may be varied in the weld deposit by the use of nickel- or iron-powder additions to the flux coating of the electrodes.

The tests were made on ferritic S.G. iron to the 60–45–10 section of A.S.T.M. specification A. 339–51T, and on grey cast iron. All test weld blocks were examined, in the as-welded condition, by metallographic methods, and by hardness exploration over appropriate sections. The results of such examination are well illustrated by photomicrographs and charts.

The results of the test confirm previous work on welding of S.G. iron, showing that the cracking-resistance of welds made with nickel-iron electrodes is superior to that of welds made with nickel or nickel-copper electrodes. It is noted also that the S.G. iron proved to be far less sensitive to variations in weld metal and welding technique than was the grey cast iron.

The authors point out, however, that although their test results clearly demonstrate the superior crack-resistance obtained with nickel-iron electrodes, the use of nickel and nickel-copper alloy for this purpose is in some instances justified. In all cases careful consideration should be given to welding conditions and service applications before choice of electrode is made. Due regard must be paid to the significance of such factors as the size and shape of the casting, welding position, preparation of joint, the skill of the operator, and the end-use of the welded component.

Nickel in Cast Irons for Enamelling

P. TYVAERT and R. PIVA: 'The Effect of Small Amounts of Nickel on the Suitability of Cast Iron for Powder-Enamelling.'

Fonderie, 1957, vol. 137, June, pp. 260–4.

Chance defects in powder-enamelled coatings on cast-iron articles such as fireplaces and sanitary equipment have frequently been attributed to the

effect of small amounts of impurities accidentally introduced into the iron during melting. The present paper reports an investigation made to determine the validity of such a theory. Since nickel is one of the most usual constituents of alloy cast irons, the authors studied the effect of that element up to a maximum of 0·5 per cent., i.e., in a range in which it could be regarded as an impurity.

The three intentionally alloyed irons contained, respectively, 0·10, 0·25 and 0·50, per cent. nickel; the control iron contained a normal trace amount, *viz.*, 0·05 per cent. Plates 140×140×4 mm. of each of these materials were examined. The surface preparation of the plates is described, together with the conditions in which they were powder-enamelled, to thicknesses of approximately 50–100 mm. The coatings were evaluated by visual examination, measurement of thickness (by a magnetic technique), and determination of adherence and of susceptibility to deterioration under impact (fragility test).

The results clearly indicate that nickel in the amounts studied has no detrimental effect in cast iron used for powder enamelling. The appearance of all the coatings was normal and their adherence was classified as excellent.

CONSTRUCTIONAL STEELS

Inter-Relation of Microstructure and Tensile Properties in Nickel Steels

J. P. HUGO and J. H. WOODHEAD: 'Correlation of Tensile Properties with Microstructure for some 3 per cent. Nickel Steels.'

Jnl. Iron and Steel Inst., 1957, vol. 186, June, pp. 174–88.

Report of study of the relationships between the isothermal transformation temperature and the tensile properties of 3 per cent. nickel steels containing, respectively, 0·67, 0·55 and 0·32 per cent. of carbon. In the pearlite range confirmation was obtained of the theory that the interlamellar spacing of pearlite is inversely proportional to the degree of undercooling. Thus, by relating all properties to the degree of undercooling, rather than to the transformation temperature, the effect of interlamellar spacing was determined. It is also shown that for pearlitic steels, after allowing for the effects of pro-eutectoid ferrite, the strength properties are linearly dependent on the square root of the interlamellar spacing, a relationship which is in accordance with dislocation theory. The results may also be related empirically to the logarithm of the interlamellar spacing. No simple relationship appears to exist for the strength properties of bainitic steels, nor for the ductility of the steels in either the pearlitic or the bainitic state.

Precipitation-Hardening Ultra-High-Strength Steel

S. J. ROSENBERG: 'New Ultra-High-Strength Steel.'

Materials and Methods, 1957, vol. 45, May, pp. 145–6.

Details are given of the composition and properties of a new steel developed at the National Bureau of Standards. Like other investigators, the metallurgists at the Bureau adopted the low-alloy nickel-chromium-molybdenum (S.A.E. 4340) type as a basis for study, and the programme of research covered (1) modifications of composition by additions of small amounts of other elements, and (2) experimental heat-treatments, to determine the conditions producing optimum strength combined with a good degree of ductility.

The composition finally selected is as follows: carbon 0·40, silicon 1·60, manganese 0·75, nickel 1·80, chromium 0·85, molybdenum 0·30, titanium 0·10, boron 0·002, per cent. (The authors note that boron was investigated because previous work at the Bureau had shown its beneficial influence on the low-temperature impact properties of high-strength steels. Since, however, the effect of boron tends to be lost unless the nitrogen present is combined, titanium was added to effect such combination.)

Study of the effects of various cycles of heat-treatment led to the choice of a straight quench followed by double tempering, a procedure which was found to give the best impact values both at room temperature and at −40°F. (−40°C.). The properties listed below are quoted as typical of the steel in the heat-treated condition.

Ultimate Tensile Strength	285 000 p.s.i. 127 t.s.i.
Yield Strength (0·2%) ..	235,000 p.s.i. 105 t.s.i.
Elongation (in 1·4 in.) ..	10%
Reduction of Area ..	35%
Charpy Impact (V-notch)	
at room temperature ..	16 ft.-lb
at −40°F. (−40°C.) ..	16 ft.-lb.

Electrolytic Polishing of Ferrous Metallographic Specimens

See abstract on p. 156.

Determination of Zirconium in Nickel-Alloy Steels

R. B. HAHN and J. L. JOHNSON: 'Determination of Zirconium in Steel: Direct Spectrophotometric Method.'

Analytical Chemistry, 1957, vol. 29, June, pp. 902–3.

The authors describe a method by which, after removal of interfering ions (by electrolysis with a mercury cathode), zirconium is determined by

measuring the absorbance of its chloranilate complex at 550 or 330 μ. It is found that results obtained by this method compare favourably with those given by the *p*-dimethylamino-azobenzenearsonic acid- and mandelic-acid methods. Results of estimation of zirconium in nickel-chromium steels are compared with values obtained by the method proposed by HAYES and JONES (*Industrial and Engineering Chemistry, Anal. Edn.*, 1941, vol. 13, pp. 603–4).

Chromatographic Analysis

See abstract on p. 156.

Microchemical Analysis: Reference Data

See abstract on p. 157.

Steels for Lead Pots

See abstract on p. 172.

HEAT- AND CORROSION-RESISTING MATERIALS

Structural Examination of Precipitation-Hardening Nickel-Chromium Alloys

W. C. BIGELOW, J. A. AMY and L. O. BROCKWAY: 'Electron-Microscopic Identification of the γ′ Phase of Nickel-base Alloys.'

Proc. Amer. Soc. Testing Materials, 1956, vol. 56, pp. 945–53.

The authors emphasize the desirability of developing improved etching procedures which will facilitate identification of minor structural phases by electron microscopy. The difficulties inherent in evolving a satisfactory technique are briefly discussed, and it is noted that two approaches have been made to the problem: (1) the use of reagents leaving, on the minor-phase particles, loosely adherent chemical products which can be picked up by surface replicas and used as a basis for identification, or (2) the use of reagents which would preferentially attack certain minor phases, so that the resulting differences in the shape or relief of the particles could readily be detected in the electron microscope by the use of shadowing techniques.

The authors describe a development of the second type, which has been found suitable for examination of the intermetallic phase γ′ found in nickel-chromium-base alloys hardened with aluminium and titanium. This phase is generally considered to have a structure based on that of the Ni_3Al constituent of the nickel-aluminium system, and it therefore differs significantly from the carbide and nitride phases with regard to susceptibility to chemical attack. This difference is utilized in the procedure described in the present paper. The reagent used preferentially dissolves the γ′ particles, but does not attack the carbides and nitrides, and surfaces so treated show depressions at the locations of the γ′ phase, while carbide and nitride particles remain in relief.

The procedure recommended usually (though not invariably) involves a preliminary etching of the specimens with reagents which preferentially attack the matrix and leave the particles of carbide and nitride phases protruding from the surface. Reagents A and B shown in the table below have been found suitable for this purpose. Selective attack on the γ′ particles is then achieved by etching with reagent C, and comparison of the micrographs after such etching, with those taken after the preliminary treatment, permits determination of the size, shape and distribution of the γ′ particles. In all cases the etching is carried out electrolytically. Treatment in solutions A or B is usually for 3–10 seconds and the time in solution C is less than 1 second. Care should be taken to avoid over-etching. As a preliminary, either mechanical polishing (with normal precautions to avoid disturbance of the structure by cold work) or electrolytic polishing is suitable. For electro-polishing good results have been obtained on several types of nickel-base alloy by using a solution consisting of 90 parts of glacial acetic acid to 10 parts of perchloric acid (70–72 per cent.).

Table I
Composition of Etching Reagents

Reagent		Ml.
A	Hydrofluoric acid (48%)	5
	Glycerol	10
	Ethyl alcohol	85
B	Phosphoric acid (85%) ..	12
	Sulphuric acid (96%) ..	47
	Nitric acid (70%) ..	41
C	Hydrofluoric acid (48%)	5
	Glycerol	10
	Ethyl alcohol	10—50
	Water .. to make	100 total volume

It is noted that reagents A and C are both modifications of the solution proposed by FLOYD and TAYLOR (*Jnl. Inst. Metals*, 1952–53, vol. 81, p. 25). The advantages of substituting part or all of the water by ethyl alcohol are discussed, as affecting clarity of delineation of γ′ phase and as giving a wider variety of selective action of the etchant.

The paper contains typical electron micrographs illustrating etching effects obtained with three typical nickel-base alloys, Inconel X, Waspalloy and Udimet: see Table II on page 169.

In commenting on the type of alloys containing the γ′

phase, the authors make the following observations:

'The intermetallic γ' phase has been observed in aged specimens of all the commercial alloys of this type studied to date. While wide variations occur in their size, shape, and distribution, the γ' particles appear to form predominantly within the matrix grains. Precipitation of appreciable amounts of this phase at the grain boundaries has been observed only in specimens of the Udimet alloy, and is thought to be related to the higher titanium and aluminium content of this alloy. Titanium-nitride particles and, in the case of alloys containing niobium, niobium-carbonitride particles, are present in these alloys even after solution treatment at 1975°-2050°F. (1080°-1120°C.) and water-quenching. These particles are randomly distributed and increase in size with subsequent ageing. Grain-boundary precipitates are not present in the solution-treated, water-quenched specimens, but develop on ageing. Such precipitates appear to consist predominantly of complex carbides of the $M_{23}C_6$ type, but may include some of the titanium-nitride and niobium-carbonitride phases.'

ultimately produces the maximum degree of embrittlement for the alloy ranges studied. The largest amount of sigma and the lowest impact values occur in alloys having the highest chromium and the lowest nickel contents.

'Cold working increases the rate of sigma formation. This increase probably results from the activity attending the recrystallization which follows the re-heating of cold-worked metal; the phase stable at the recrystallization temperature, which is sigma, forms most readily. Thus, sigma formation in cold-worked material is nearly completed in only 100 hours at 1200°F. (650°C.), whereas in annealed material it appears to be far from completed after 3,000 hours at that temperature.'

In the alloys used for the above correlations, the silicon content was in all cases of the order of 0·7 per cent., with carbon about 0·5 and manganese about 1·9 per cent., but, in view of the known effects of silicon on formation of sigma phase, the authors give specific attention to the influence of that element. Among the observations made were the following.

With 0·7 per cent. silicon neither the 20–35 nor

Table II

Compositions of the Precipitation-Hardening Nickel-base Alloys Studied

Alloy	Ni %	Cr %	Co %	Fe %	Mo %	Ti %	Al %	Nb %	Mn %	Si %	C %
Inconel-X	73·4	14·6	—	6·90	—	2·33	0·67	1·04	0·51	0·39	0·05
Waspalloy	56·5	19·5	13·4	2·90	2·81	2·21	1·09	—	0·88	0·62	0·09
Udimet	55·4	19·5	14·8	—	3·80	2·79	2·94	—	0·17	0·50	0·08

Sigma Formation in Nickel-Chromium-Iron Alloys

F. B. FOLEY and V. N. KRIVOBOK: 'Sigma Formation in Commercial Ni-Cr-Fe Alloys.'

Metal Progress, 1957, vol. 71, May, pp. 81-6.

The authors have assembled available information on the formation of sigma phase in iron-nickel-chromium alloys, and, by correlating the data, have constructed three-dimensional figures showing the mutual influence of nickel and chromium on the amount of sigma formed and, consequently, on the toughness of wrought commercial-type alloys, (*a*) cold-rolled, or (*b*) quench-annealed, after exposure for periods varying up to 3,000 hours at temperatures at which sigma is liable to form (1200°, 1475° and 1650°F.; 650°, 800° and 900°C. approx.).

For full appreciation of the information presented, the figures in the original must be consulted. The authors summarize their findings as follows:

'After long exposure at 1200°F. (650°C.), i.e., 3,000 hours and perhaps longer, ferrous alloys containing 15–30 per cent. of chromium together with 20–35 per cent. of nickel probably transform in some degree to sigma phase. This temperature

the 20–25 chromium–nickel–iron alloys, annealed or cold-worked, showed sigma after exposure at any of the test temperatures, whereas in the 20–35 per cent. alloy containing 3 per cent. of silicon sigma appeared in both the annealed and the cold-worked specimens after the 3,000-hour treatment at 1200°F. (650°C.), and in the 20–25 per cent. alloy sigma was formed in the 3 per cent. silicon material after 3,000 hours at both 1200° and 1475°F. (650° and 800°C.). In a 25–20 chromium–nickel–iron alloy increase in silicon from 0·2 to only 0·7 per cent. greatly increased sigma formation at all temperatures, especially at 1475°F. (800°C.). While cold working promotes sigma in nickel-chromium-iron alloys in the lower part of the temperature range, it also increases the tendency of the sigma to transform back to either gamma or alpha at higher temperatures: both transformations are more sluggish in the unworked metal. If the cold-worked metal is nearly recrystallized prior to the disappearance of the sigma phase, transformation to alpha (or to gamma, as may be) may still be accelerated by the nucleation to be expected during completion of recrystallization.

With regard to the influence of basis composition,

nickel appears to lower the temperature at which sigma forms and to narrow the range of temperature in which it is stable. For example, in a cold-worked high-silicon alloy containing 35 per cent. of nickel sigma is present only after exposure at 1200°F. (650°C.): in the 25 per cent. nickel alloy it is found after exposure at both 1200° and 1475°F. (650° and 800°C.) and in a 20 per cent. nickel alloy treatment at all three temperatures 1200°, 1475° and 1650°F. (650°, 800° and 900°C.) caused sigma to form.

Influence of Hot-Working Conditions on High-Temperature Properties

J. F. EWING and J. W. FREEMAN: 'Influence of Hot-Working Conditions on the High-Temperature Properties of Heat-Resistant Alloys.'
Proc. Amer. Soc. Testing Materials, 1956, vol. 56, pp. 756–88.

The very wide scatter observed in the properties of high-temperature alloys in the hot-worked condition has indicated the need for closer study of the influence of this stage of processing. The work reported in this paper is a contribution to the systematic investigation of the subject.

The study applies primarily to austenitic alloys which are dependent upon solution annealing or hot-cold working for attainment of optimum strength at elevated temperatures, *not* with materials in which strong age-hardening reactions are utilized for that purpose. The alloy selected for examination as typical was of the following composition: carbon 0·15, silicon 0·50, manganese 1·5, chromium 20, nickel 20, cobalt 20, molybdenum 3, tungsten 2, niobium 1, per cent., balance iron. The influence of variation in hot-working conditions was evaluated by creep-rupture and creep tests at 1200° and 1500°F. (650° and 815°C.): hardness tests, metallographic examination and measurements of lattice parameter were used to establish structural effects associated with the respective conditions of the alloy.

Among the conclusions drawn from the extensive experimental data recorded for the individual series of tests are the following:

'During hot working at constant temperature only limited amounts of reduction can be introduced before further working results either in lowering of high-temperature strength, or at best confers no further increase. For rupture strengths to 1000 hours at 1200°F. (650°C.) the optimum hot reduction for this material was 15 per cent., irrespective of the temperature of working. Maximum strength attained was also independent of the temperature of hot working, except when recrystallization occurred during working, or when certain precipitation reaction had previously taken place during heating for hot working. Maximum rupture strength at 1500°F. (815°C.) was constant, regardless of temperature of reduction, but the reduction associated with optimum strength varied with the temperature at which the reduction was effected.

'Very high strengths at 1200°F. (650°C.) and relatively high strengths at 1500°F. (815°C.) were characteristic when gradual reductions were made over a falling temperature range. Application of this principle permits development, with all working temperatures above 1800°F. (980°C.), of strengths equal to those normally obtained by hot-cold working at 1200°–1400°F. (650°–760°C.). Many small reductions over a falling temperature range resulted also in high ductility.

'Repeated working at abnormally low re-heat temperatures caused very low strength properties, associated with high ductility.'

The authors consider that the principles established explain many of the variations which have been observed in the high-temperature properties of alloys, and the results indicate that it should not be unduly difficult to control hot-working conditions within limits which will give improved properties.

Extensive variations in hot-working conditions did not change the response of the material to the heat-treatments commonly employed. The observations made on the structures associated with the various conditions of the alloy suggest that strain-hardening is the predominant strengthening mechanism operating during hot working. It appears likely that unidentified reactions, such as the ordering of the matrix structure, may have more effect on properties than has yet been recognized.

The observations made constitute a strong argument for the closer study of hot-working conditions as a factor in obtaining optimum combinations of strength and ductility in alloys at elevated temperatures.

Influence of Cold Work on Creep-Rupture Properties

F. B. CUFF and N. J. GRANT: 'The Effect of Cold Work on the Creep-Rupture Properties of a Series of Simple 18-8 Stainless Steels.'
Jnl. Iron and Steel Inst., 1957, vol. 186, June, pp. 188–97.

The paper describes work on a series of chromium-nickel steels which, by virtue of variation in composition, were liable to varying structural and phase instabilities. The types selected are shown in the table on page 171, with their respective M_s temperatures.

The steels were studied in four conditions: annealed, and at three levels of cold work: 15, 25, and 35, per cent. reduction. In the stress-rupture tests, which were made on all the steels at 1100° and 1200°F. (593° and 648°C.), times-to-rupture ranged from 0·01 to 1000 hours. Steel No. 3 was tested also at 1300°F. (704°C.). After testing, all specimens were examined metallographically, and in some cases the ferrite content was determined by the Magnegage. Tensile tests were also made, as a means of comparing low- and high-temperature properties. The results of the high-temperature tests on the steels in the respective conditions are presented in an extensive series of graphs. From the observations made the authors draw attention to the following points:

'The higher the M_s temperature, the lower is the recrystallization temperature and the weaker is

Table I

Steel	Cr	Ni	C	N_2	$C+N_2$	M_S	
	%	%	%	%	%	°F.	°C.
1	15·73	8·73	0·028	0·030	0·058	+100*	+38
2	16·16	9·43	0·036	0·032	0·068	−125*	−87
3	16·01	11·08	0·025	0·025	0·051	−300*	−184
4	19·11	10·60	0·020	0·022	0·042	−340†	−206
5	16·33	14·83	0·028	0·028	0·056	−627†	−366
6	21·76	13·93	0·035	0·040	0·075	−936†	−537

* Determined by the electrical-resistivity method. † Calculated values.

the steel in creep-rupture in the annealed condition. This is even more marked in the cold-worked state.

'The beneficial effect of cold work on creep-rupture properties is greatest in the stably austenitic steels, and these steels do not recrystallize at 1200°F. (650°C.) or below in less than 1000 hours.

'In long-time tests, especially above 1200°F. (650°C.) fully austenitic steels are subject to weakening if carbide agglomeration occurs or if sigma phase is formed. The occurrence of such effects suggests the advisability of using steels of low carbon+nitrogen content, with enough nickel to ensure stabilization, and chromium at levels which are high, but not sufficiently so to cause formation of sigma. Other alloy additions should be selected with due regard to preservation of a stable austenite of high recrystallization temperature, and prevention of carbide precipitation or formation of sigma. Low creep-rupture ductility is associated with strengthening obtained by cold work, but significant increase in ductility occurs with recrystallization during test.

'Room-temperature tests showed that response to cold work, i.e., increased strength, improves with increasing amounts of martensite initially present in the steel.'

Cracking in High-Temperature Alloys during Creep

D. McLEAN: 'A Note on the Metallography of Cracking during Creep.'

Jnl. Inst. Metals, 1957, vol. 85, July, pp. 468–72.

Until recently it was generally believed that intergranular cracks generated during creep always originated at corners of the grains, but it has now been demonstrated that cavities, which combine to form cracks, may occur at any point along the grain boundaries. It appeared possible that the explanation of this apparent contradiction might be that the starting point of the crack depended on the conditions of test, and the work carried out by the present author was planned to investigate this possibility.

Tests were made on some typical high-temperature materials, viz., Nimonic 90 (nickel-chromium-cobalt-base alloy), Nimonic 80 and 80A (nickel-chromium-base alloys), G.32 (complex cobalt-chromium-nickel-iron alloy) and R.ex 337A (austenitic chromium-nickel steel containing copper and molybdenum). These materials were broken in creep tests, at various stresses and temperatures, and were examined with regard to the inception of fracture in the various conditions of test.

With the exception of Nimonic 80, in which few cracks were formed, the observations made on all the materials gave a consistent and clear demonstration of the cracking phenomenon. Stress appears to be the main controlling factor. At low stresses fracture originates by formation of isolated cavities which lie mainly in transverse grain boundaries: at high stresses fracture starts with cracks which appear to be produced by relatively large concentrations of stress. In R.ex 337A the cracks lay inside the grains, often remote from grain boundaries, but in the other materials they were located at grain corners. The minimum stress required to cause cracking is sufficiently below the calculated minimum value to make it likely that cohesion in the alloys is lower than that characteristic of pure metals. The author suggests that if such is the case the probable reason is that alloying elements or impurities reduce the surface energy of the material.

Relaxation Properties of Nickel-Alloy Spring Materials

R. G. MATTERS and R. E. LOCHEN: 'Materials for Helical Compression Springs for Use at Constant Deflection from 600° to 1400°F.'

Proc. Amer. Soc. Testing Materials, 1956, vol. 56, pp. 672–83; disc., pp. 683–6.

Following a brief review of the somewhat sparse data available on relaxation behaviour of spring materials at elevated temperature, the authors report results of a long-term study which has been made

in the laboratories of the Allis-Chalmers Manufacturing Company, on materials for use as helical springs under constant deflection conditions. For the specific application envisaged the springs may relax, but must support a specified minimum dead load.

The relationships between torsional stress and torsional strain of a spring under relaxation with a fixed deflection are diagrammatically shown, and an explanation is given of the methods used for evaluation of torsional elastic recovery and of load-carrying capacity at given deflection after relaxation has occurred.

The work reported comprised a comparison of the relaxation properties of high-speed steel, which, at the time the research was started, was one of the best materials available for service above 600°F. (315°C.); annealed Inconel (nickel-chromium-iron alloy); cold-drawn 18-8 chromium-nickel steel; cold-drawn Timken 16-25-6 chromium-nickel-molybdenum steel, cold-drawn 19-9 DX (chromium-nickel steel containing molybdenum and tungsten); S-816 (cobalt-base alloy containing 20 per cent. each of nickel and chromium, together with smaller amounts of molybdenum, tungsten and niobium); Elgiloy (precipitation-hardening nickel-chromium-iron alloy), and A-286 (austenitic chromium-nickel steel).

The results are presented on the basis of an effective residual stress calculated from the recovery of the spring when the restraint was released, a criterion which is considered to be practically useful for design purposes under conditions of only moderate relaxation. Of the nine materials tested, S-816 showed the best resistance to relaxation, and it is believed that springs of this material would be useful at temperatures up to about 1200°F. (650°C.). At 1000°F. (540°C.) the relaxation-resistance of Inconel X and of A-286 approached that of S-816, and at still lower temperatures severely cold-drawn austenitic steels also show useful spring properties.

Elevated-Temperature Properties of Cast Irons

See abstract on p. 165.

Oxidation of Nickel-Iron Alloys

See abstract on p. 164.

Steels for Lead Pots

H. KRAUTMACHER and W. PÜNGEL: 'The Life of Containers for Molten Lead.'

Stahl und Eisen, 1957, vol. 77, June 27, pp. 837–45.

In the wire-working industry lead baths are used for both patenting and annealing. For operations involving temperatures of the order of 500°–550°C. a satisfactory life is obtained from the pots, which are usually made from steel sheet, but pots used for annealing at higher temperatures, e.g., 700°–740°C., fail by corrosion after unduly short periods, necessitating frequent replacement.

This paper contains a comprehensive review of information culled from the literature, from laboratory tests, and from tests under commercial conditions. The main conclusions drawn are that the corrosive attack depends mainly on the temperature of the lead bath, and to a lesser degree, on the duration of exposure. It was noted that, of the unalloyed and low-alloy types studied, killed steel was more resistant than rimmed steel, and it is recommended that where unalloyed steel is used the killed grade should be employed. Further precautions which assist in prolonging life include avoidance of localized overheating of the pots, prevention of mechanical injury to the coating of scale which forms on the inside of the pots, and provision of a protective gas atmosphere, to lessen formation of lead oxide.

Tests under large-scale industrial conditions (300 hours in lead baths at 720°C.) included experiments with high-chromium and chromium-nickel steels of corrosion- and heat-resisting types. These materials showed outstandingly high resistance to deterioration, indicating a life of many years. While it is realized that fabrication of such containers from solid corrosion- and heat-resisting steels would be uneconomic, it is suggested that consideration should be given to the use of the higher-alloy steels in the form of cladding for both the inner and outer surfaces of the pots. The tests made in this investigation were carried out on two high-alloy materials only, but further study of the most suitable materials for cladding could well be of ultimate economic value to the industry.

Copper-Nickel Heat-Exchanger Tubes

See abstract on p. 163.

Stainless Steels: Production, Properties, Uses

'Special Stainless Steel Issue.'

Metal Bull., July 1957: 70 pp.

The publication of this special issue is designed to draw attention to the rapid strides which have been made in the stainless steels since their introduction some fifty years ago. Particular emphasis is laid on the widely varying properties which can now be obtained in these steels by appropriate modification of composition and heat-treatment, and of the resulting extended use of such materials in many fields. Individual items in the series forming the review include descriptions of modern production and fabrication methods used by producers of stainless steels, a record of service experience in the use of stainless steels in domestic, engineering, architectural and other applications, and reports on the stainless-steel industry in the U.K., the U.S.A. and Canada, France, Sweden and Japan.

Reference information included covers a list of stainless-steel producers in the U.K., with notes on the types of product manufactured by the respective firms.

Boron Additions to Stainless Steels

D. L. LOVELESS and F. K. BLOOM: 'Boron Solves Hot-Shortness in Stainless Steel.'

Iron Age, 1957, vol. 179, June 20, pp. 95–7.

This article draws attention to the beneficial effect,

on hot-workability, of adding small amounts of boron to austenitic chromium-nickel steels of both simple and complex types. The improvement is particularly marked in the case of the higher-alloy grades, which tend to be hot-short in certain temperature ranges, and hence prone to cracking or tearing under rolling or forging operations. The information given is based on experience in the Baltimore works of Armco Steel Corporation, where the influence of boron was first observed during a study of flux additions to moulds. It was found that when small quantities of rasorite ore (sodium tetraborate) were added during pouring the resultant ingots showed a remarkable improvement in hot-workability, and the effect was enhanced by making such additions in the ladle. The improvement attainable is demonstrated by comparison of results of hot-bend ductility tests on boron-treated and boron-free standard A.I.S.I. austenitic chromium-nickel steels varying from 18-8 to 25-20 types, and on a complex 20-28 type containing copper and molybdenum.

It is stated that any convenient source of boron may be used to make the addition: oxides, borides or ferroalloys are suitable; best results are obtained if the boron addition agent is used in association with deoxidizing media such as calcium-silicon or ferro-titanium. There is also some indication that combined treatment with boron and rare earths or rare-earth oxides is preferable to the use of rare earths only.

The amount of boron added need not be large: for example, a boron content of 0·0005 per cent. in an 18-8 chromium-nickel steel increases the hot ductility by as much as 50 per cent. Large additions of boron are, indeed, detrimental, since boron appears to have a relatively low solubility in the austenitic steels. When the boron content exceeds about 0·002-0·005 per cent. faint traces of an intermetallic boride are found, and at more than 0·010 per cent. boron the amount of the boride becomes appreciable and assumes a eutectic appearance. The presence of such a eutectic constituent has a disastrous effect on hot ductility.

Boron treatment has proved beneficial also for the modified high-manganese, low-nickel austenitic steels, e.g., in a steel of the Armco 21-4 grade which contains carbon 0·55, manganese 8·50, chromium 20·50, nickel 3·50, nitrogen 0·40, per cent.

The mechanism of the improvement so obtained is still under study, but experience to date leads to the suggestion that boron may have two effects: (1) it may precipitate a compound of some type which is independent of the presence of carbon, and may be an intermetallic boride, and (2) it may accelerate the rate at which normal chromium carbide (or possibly boro-carbide) will precipitate during cooling of the steel from the annealing temperature. The boride precipitate does not appear to have an adverse influence on corrosion-resistance, but it is nevertheless considered preferable to limit the additions to levels which do not cause formation of boride or carbides.

Austenitic Nickel-Chromium Steel in Aerated Sulphuric Acid

G. H. CARTLEDGE: 'The Activation and Passivation of Stainless Steel in Aerated Sulphuric Acid.'
Jnl. Electrochemical Soc., 1957, vol. 104, July, pp. 420-6.

The work described in this paper was undertaken as an introduction to study of the mechanism of the action of a variety of substances on the electrochemical behaviour of stainless steel in acidic solutions.

Potential-time curves were determined, at 85°C., for a niobium-stabilized stainless steel during its transition to the state which is essentially stable in 0·1*N* sulphuric acid. Experiments were carried out on both pre-oxidized specimens and on specimens which had previously been saturated with hydrogen by electrolysis.

It was found that the potential passes through characteristic changes, and an attempt was made to relate the inflections found to the behaviour of the metal at those stages. In particular it was found that, in the conditions used, there is a 'critical recovery potential' above which spontaneous passivation occurs. This potential is shown to be approximately equal to the hydrogen potential for identical conditions. It was observed that the corrosion rate of the steel was characteristically related to the changes in potential.

Resistance of Stainless Steels and High-Nickel Alloys to Corrosion in Supercritical Water

W. K. BOYD and H. A. PRAY: 'Corrosion of Stainless Steels in Supercritical Water.'
Corrosion, 1957, vol. 13, June, pp. 375t-84t.

This paper reports the results of an investigation carried out to determine the corrosion-resistance of a number of stainless steels and alloys in high-purity water, a problem which has assumed new significance with the advent of water-cooled nuclear reactors.

The materials tested were high-chromium stainless steel, four grades of austenitic nickel-chromium steel (A.I.S.I. Types 302, 347, 309 and 310), three precipitation-hardening grades (Armco 17-4 P.H., Armco 17-7 P.H. and Allegheny A-286), Inconel X (precipitation-hardening nickel-chromium-iron-base alloy), Hastelloy F and Hastelloy X (nickel-chromium-molybdenum-base alloys) and AMS 5616 (a high-chromium steel containing small percentages of nickel and tungsten). The hardenable grades were solution treated and aged, and the steels of the Type 300 series were quench-annealed from 2000°F. (1093°C.). Full details are given of the compositions of the materials tested.

Each material was evaluated in de-gassed supercritical water at 1350°, 1000° and 800°F. (732°, 538° and 426°C.) at a pressure of 5000 p.s.i., for times up to 148 days. (In general, any material showing a weight change of less than 100 mg/dm²/130 days, and having a tarnish film or thin oxide layer, was considered satisfactory.) In addition, the

behaviour of selected materials was determined in de-gassed water at 1000°F. (538°C.) in the presence of hydrogen, and the effect of applied stress, on corrosion-resistance, was also studied. Details are given of test procedure and apparatus, together with data on weight-gain, and photomicrographs of the specimens after various test periods.

From the results, the authors conclude that Hastelloy F and Armco 17-4 P.H. and 17-7 P.H. are the materials most likely to give adequate service in de-gassed supercritical water at 1350°F. (732°C.). As the temperature is lowered to 1000° and 800°F. (538° and 426°C.) the choice of materials becomes considerably greater: at 1000°F. only Allegheny A-286, Inconel X, and straight 18-8 chromium-nickel stainless steel were seriously attacked, and at 800°F. all the materials tested showed acceptable resistance to corrosion. At 1350°F. (732°C.) attack was localized and selective, even in the case of the materials considered to have good resistance to corrosion. Some decarburization was also noted after tests at this temperature, but at 1000°F. (538°C.) and below the corrosion attack was more uniform.

When stainless steels are exposed under stress to de-gassed supercritical water the possibility of stress-corrosion cracking must be considered: this effect was observed in supplementary tests in which two types of stainless steel were exposed under a constant stress of 90 per cent. of the value required to cause rupture in 1000 hours. Such conditions, after one week's exposure, caused failure of an 18-8 chromium-nickel steel containing 2-3 per cent. of molybdenum (Type 316), whereas a higher-molybdenum grade (Type 317) was still intact. Examination of the failed specimen showed many fine cracks, in addition to the main fracture: the cracks were primarily transgranular and appeared generally to be associated with a small corrosion pit.

Stress-Corrosion Cracking of Nickel-Chromium Stainless Steels in the Presence of Chlorides

H. R. COPSON and C. F. CHENG: 'Some Case Histories of Stress-Corrosion Cracking of Austenitic Stainless Steels Associated with Chlorides.'

Corrosion, 1957, vol. 13, June, pp. 397t-404t.

It is generally recognized that, under certain conditions, austenitic stainless steels are susceptible to intergranular stress-corrosion cracking in chloride solutions. Cracking has been reported not only in hot, concentrated solutions, but also when the chloride concentration was initially quite dilute. References in the literature to service failures of this type are infrequent and brief, but this paper describes 22 case histories which have been investigated in the laboratories of The International Nickel Company. All were concerned specifically with stress-corrosion cracking of stainless steels in contact with chlorides, under varying conditions.

The steels studied include straight chromium-nickel types, niobium- and titanium-stabilized grades, and chromium-nickel steels containing small amounts of molybdenum. Six of the cases mentioned involved exposure to water which evaporated, giving rise to increased chloride concentration; four involved exposure to steam, three to brines and the remainder to various other conditions, of which full details are given. In each case either the chloride content was initially high, or conditions of operation were such that a dangerous concentration could develop. In several instances the environment was acid, and in most cases it appeared likely that air had been present. Usually the service temperatures had been relatively high. The periods elapsing before failure varied from a few days to a few years.

Full particulars of the condition and nature of the failures are given. In all cases microexamination revealed transcrystalline cracks, which usually exhibited a characteristic branching growth.

Based on the observations made, various practical suggestions are put forward for avoidance of stress-corrosion cracking, e.g., by suitable design of components, by avoiding concentration of chlorides, by control of the oxygen content of the solutions and their temperature, by cathodic protection, and by the use of corrosion-resisting materials of construction. In the last-named connexion, a report is made of stress-corrosion cracking tests carried out on a series of high-nickel alloys exposed in various mixed-chloride solutions. The results indicate that elements which tend to stabilize austenite (e.g., nickel and copper) are helpful in conferring increased resistance, whereas those which tend to stabilize ferrite (e.g., molybdenum, chromium and titanium) are harmful. Particular attention is called to the satisfactory resistance of Inconel (nickel-chromium-iron alloy), which gave specially good results in the laboratory tests and which, so far as is known, has never suffered this type of stress-corrosion cracking. The authors conclude that although field tests will be necessary to delimit composition more closely, it is safe to conclude that the more drastic the conditions of service, the higher will be the nickel content required to prevent failure of the alloys.

Intergranular Corrosion-Resistance of Chromium-Manganese-Nickel Steels

W. O. BINDER, J. THOMPSON and C. R. BISHOP: 'Intergranular Corrosion-Resistance of Low-Carbon Austenitic Chromium-Manganese-Nickel Steels.'

Proc. Amer. Soc. Testing Materials, 1956, vol. 56, pp. 903-20; disc., pp. 920-2.

The austenitic chromium-manganese-nickel steels become susceptible to intergranular corrosion when heated in the temperature range 425°-815°C., and the introduction of niobium or titanium as stabilizers results in metallurgical complications. The formation of delta ferrite (due to removal, by the stabilizers, of carbon and nitrogen from solution) may lead to difficulty in hot working, and subsequent transformation of delta ferrite to sigma phase, when the steel is exposed to elevated temperatures, may produce brittleness, and lower the corrosion-resistance

of the steels. In the lower-nickel steels of the series, when titanium is present the austenite is liable to transform into low-temperature ferrite, and the steel may lose its non-magnetic characteristics.

The above considerations prompted investigation of the possibility of obviating intergranular corrosion by reducing the carbon content of the steels. In such compositions a fully austenitic condition can be secured by increasing the nitrogen content, a modification which does not promote intergranular corrosion. The development of steels having a maximum possible tolerance for carbon is, however, commercially desirable, and the investigation reported in this paper was undertaken to determine the influence of composition on the resistance of the steels to intergranular corrosion, with particular reference to the permissible carbon range.

The steels investigated contained chromium 18, manganese 7–11, nickel 4–10, silicon 0·4, nitrogen 0·22, per cent., with carbon 0·015–0·05, per cent. With one exception, they contained more manganese than nickel.

Corrosion-resistance was evaluated by tests in boiling 65 per cent. nitric acid, boiling acidified copper-sulphate solution, and a mixed solution containing 10 per cent. of nitric acid and 3 per cent. of hydrofluoric acid (used at 70°F.; 21°C.). In all cases the specimens tested had been heated for various periods at temperatures in the range 300°–650°C., to induce susceptibility to intergranular attack. Susceptibility was rated on the basis of the ratio of the corrosion rate after heat-treatment to that in the solution-treated condition (1075°C., air-cooled), and the steel was considered to have failed if that ratio exceeded about 1·25. A detailed record is made of the results of the tests.

It was found that the maximum carbon content at which the steels retain immunity to intergranular corrosion is related to the sum of the manganese and nickel contents: carbon tolerance decreased as the sum of these two elements increased above 14 per cent. Steels containing about 0·05 per cent. carbon and up to 14 per cent. manganese+nickel, or about 0·035 per cent. carbon and 18 per cent. manganese+nickel are resistant to intergranular attack after 1 hour at 650°C. Those containing 0·02–0·025 per cent. carbon and 14 per cent. manganese+nickel or about 0·02 per cent. carbon and 18 per cent. manganese+nickel are resistant after 24 hours at 650°C. Since current arc-melting practice limits carbon to about 0·025 per cent. minimum, complete immunity (as indicated by resistance after heating for 24 hours at 650°C.) imposes a limit of 14 per cent. manganese+nickel, and the economics of melting also suggest that a similar limit should be applied to steels which meet the immunity requirements after 1 hour at 650°C. The carbon limits for partial immunity are, however, less stringent than those essential to secure complete freedom from susceptibility.

Steels resistant after 1 hour at 650°C. should, it is considered, be satisfactory in many applications, for use in the as-welded or stress-relieved conditions, and those satisfactory after 24 hours at 650°C. should be suitable for continuous service at temperatures in the carbide-precipitation temperature range. Although limited to short periods of exposure in the higher temperature ranges, steels meeting the requirements for satisfactory behaviour after 1 hour at 650°C. may be continuously heated at temperatures as high as 400°C. without danger of becoming susceptible to intergranular attack.

Stainless-Steel Tanks for Shipping Orange Juice

'Tropicana Transports Orange Juice in Huge Stainless-Steel Tanks.'

Nickel Topics, 1957, vol. 10, No. 6, pp. 1, 3.

Orange juice from Florida, with flavour and vitamin content unimpaired, is now being delivered in bulk in the U.S.A. and Canada by use of tank transport by sea. The S.S. 'Tropicana', a cargo ship owned by Fruit Industries Inc., Florida, has been fitted with stainless-steel tanks varying in capacity from 30,000 to 90,000 gallons each (total capacity 650,000 gallons). Tests by the U.S. Department of Agriculture have proved that in the vacuum-sealed refrigerated tanks the juice would keep in perfect condition for more than seven weeks, i.e., a period much longer than the few days involved in transport. Each tank is insulated with 6½-in. foam glass, to maintain the juice at the optimum temperature of 28°–30°C. during transport.

The 18-8 chromium-nickel type of steel which is used for the tanks has been selected also for the other vessels, pipes, etc., which handle the juice during its journey from the Florida plant where the juice is first extracted, through to the receiving stations. The same material is used for the trucks in which the juice is delivered to the distributors.

The development has already proved so successful that the 650,000-gallon capacity of the 'Tropicana' is to be increased to 1,450,000 gallons as soon as the necessary tanks can be installed.

Nickel-Lining of Steel Vessels

J. L. WEIS: 'Nickel-Lined Steel Vessels for Caustic Service.'

Industrial and Engineering Chemistry, 1957, vol. 49, June, pp. 69A–70A.

For economic reasons vessels of carbon steel are used whenever possible in the manufacture and handling of sodium hydroxide, and, within limits, give satisfactory service. Above certain temperatures and caustic concentrations, however, the steel is highly susceptible to stress-corrosion cracking and fails after short service. In this article the author describes a salvage method (developed at the Deer Park Plant of Diamond Alkali Company) by which failed vessels can be restored to a mechanically sound condition by welding, and protected against further corrosion by lining with nickel sheet.

The procedure used, evolved as a result of much experimental work, is illustrated with reference to a cone-bottom salt settler, operated at a temperature of approximately 200°F. (93°C.), in conditions

involving thermal and pressure-vacuum cycling. The method, where suitable, can save up to fifty per cent. of the cost of a new vessel.

S.G. Iron in Marine Applications

See abstract on p. 165.

Mechanical Polishing of Stainless Steel: Deformation during Abrasion

L. E. SAMUELS and G. R. WALLWORK: 'The Nature of Mechanically Polished Metal Surfaces. Deformation Produced during Abrasion of 18-8 Type Austenitic Steel.'

Jnl. Iron and Steel Inst., 1957, vol. 186, June, pp. 211-18.

The work reported in this paper is a sequel to investigations of a similar character on 70-30 brass (to be published). For the equipment and methods employed, reference is directed to *Metallurgia*, 1955, vol. 51, pp. 161-2. The present paper contains the results of observations made, by a metallographic taper-sectioning technique, of the structure of the deformed surface layer produced during abrasion of an austenitic chromium-nickel steel. The depth of the disturbed layer produced by various methods of abrasion employed in metallographic practice was systematically investigated, and the optimum conditions (i.e., those producing minimum deformation) were established.

The results, which are stated to be in good agreement with those obtained on brass, confirm that the gross deformation which is frequently reported as being present in mechanically polished surfaces of metastable austenitic steels originates during the preliminary abrasion stages of preparation and that such interference can be reduced to an acceptable level by suitable mechanical methods of polishing. Recommendations are made with regard to optimum condition of the polishing papers used, and the time and other variables of the polishing operations.

The work has also indicated that machining operations of the type frequently necessary for preparation of a flat surface prior to polishing are also a possible source of the gross deformation found in the finished surfaces. Such operations should therefore be carried out in conditions ensuring minimum disturbance of the remaining surface, and the first stage of the abrasion used in preparation of metallographic specimens must be such as to remove as far as possible the deformed surface layer. This can be best achieved by cutting at the maximum possible rate in the first abrasive stage, using a coarse silicon-carbide paper, in a comparatively fresh condition and under maximum pressure.

High-Vacuum Furnace Brazing of Nickel Alloys

'High-Vacuum Furnace Brazing.'

Welding and Metal Fabrication, 1957, vol. 25, June, pp. 212-14.

The article describes equipment and technique used in a new method of brazing stainless steel, high-nickel alloys such as Inconel and the Nimonic alloys, and titanium. The process is described as used in the laboratories of Messrs. Joseph Lucas, Ltd., Birmingham.

In some applications of such materials high-temperature brazing has been recognized for some time as a useful method of assembly, and high-melting-point filler materials of various types have been developed for this purpose, e.g., silver-palladium-manganese, nickel-chromium-boron, nickel-silicon-boron, and nickel-chromium-manganese alloys.

Until recently the high temperatures required (of the order of 1120°-1250°C.) have been obtained by ordinary furnace brazing and the assembly has been held in a separate chamber. In this method of brazing an atmosphere of cracked ammonia or hydrogen is usually required, and unless pure dry hydrogen can be employed, a suitable brazing flux must be introduced. With the new high-vacuum brazing furnace, however, no flux is necessary, thus making possible the production of clean joints without risk of flux inclusions. Associated with this development a resistance-heating technique has been evolved, by which it is possible to braze several joints of an assembly in one operation, without any distortion and without the need for subsequent internal cleaning.

The design and operation of the new furnaces are described and illustrated in this article.

Nickel-containing Alloys for Brazing Zircaloy

J. B. McANDREW, H. SCHWARTZBART and R. NECHELES: 'Corrosion-Resistance of Zircaloy-2 Brazements in High-Temperature Water.'

Welding Jnl., 1957, vol. 36, June, pp. 287S-90S.

Zirconium-base alloys characterized by low thermal neutron-capture cross-section have proved particularly resistant to attack by high-temperature pressurized water, in conditions obtaining in nuclear reactors, and there is now a need to develop brazing techniques which can be applied to such materials. The problem is a complicated one, since not only must the brazing alloy itself be resistant to corrosion under the severe conditions involved, but any alloy which may be formed in producing the joints must have a similar degree of corrosion-resistance. The fact that large additions of various elements to zirconium are known to impair the corrosion-resisting qualities of the metal limits the choice of composition possible for brazing materials.

This paper reports 'screening' tests made with a range of brazing alloys of experimental types, used to produce joints in Zircaloy 2*. The brazed joints were subjected to corrosion tests in pressurized water at 680°F. (360°C.), for periods up to (and in some cases exceeding) 1200 hours.

The brazing alloys which, in these tests, showed a promising degree of corrosion-resistance were of widely varying type, and the authors cannot formulate any theory relating composition to the behaviour of the materials. In general it can be stated that none of the aluminium alloys were acceptable;

* Sn 1·5, Fe 0.12, Cr 0.10, Ni 0.05%, bal. Zr.

silver- and gold-base alloys gave unsatisfactory results, due, it is believed, to pick-up of zirconium and formation of alloy compositions not resistant to corrosion; palladium appeared to stimulate extensive corrosion of the parent alloy, but the reason for this effect is not yet clear. The following types of alloy have been selected for further consideration:

Table II

Ni %	Cr %	Zr %	Be %	Pd %	In %	P %	Si %	Ge %	Cu %
—	—	Bal.	5	—	—	—	—	—	—
—	—	—	—	20	3	—	—	—	Bal.
Bal.	—	—	—	20	—	—	10	—	—
Bal.	13	—	—	—	—	—	—	30	—
Bal.	—	—	—	—	—	6	—	—	—

Weld Heat-Affected Zone in Niobium-Stabilized Austenitic Steel

E. F. NIPPES, B. SCHAAF, W. L. FLEISCHMANN and R. L. MEHAN: 'Time-Temperature Effect on Properties of Weld Heat-Affected Zone in Type 347 Stainless Steel.'

Welding Jnl., 1957, vol. 36, June, pp. 265S-70S.

This paper is a further contribution to the literature of base-metal cracking in the heat-affected zone of the niobium-stabilized austenitic chromium-nickel steel which is so widely used in power and nuclear reactor plant. The following aspects were specifically investigated:

The type of carbides which precipitate from the grain-coarsened supersaturated austenite of the weld heat-affected zone, on exposure of the steel to elevated temperatures.

The changes in metallurgical phases, and associated mechanical and corrosion-resisting properties, which might occur during long-term exposure of welded joints to elevated temperatures.

The significance of nickel content, which was investigated by comparing the behaviour of simulated weld-test specimens of high-nickel (12·75%) and low-nickel (9·75 and 9·59%) steels, both falling within the limits of Type 347 specification.

A limited number of tests was also made on welded joints in Type 304 steel (carbon 0·08 max., chromium 18·00-20·00, nickel 8·00-11·00, per cent.), to provide a basis of evaluation for the weldments in Type 347.

Earlier work in the authors' laboratory (Rensselaer Polytechnic Institute) had established that deterioration was liable to occur in welded joints which had attained a temperature of about 2450°F. (1345°C.) and the work reported in the present paper was therefore concentrated on the behaviour of specimens heated, in simulated welding cycles, to a peak temperature of 2450°F.

Re-heating experiments which covered time-temperature periods from 40 hours at 1000°F. (538°C.) to 1000 hours at 1300°F. (704°C.), i.e., conditions which could obtain in the relevant applications, resulted in no significant change in mechanical properties. Tests in 65 per cent. boiling nitric acid gave clear indication that corrosion of the welded joints is time-temperature dependent, and demonstrated a definite correlation between sensitizing treatment and rate of corrosion.

Welding of High-Nickel Alloys

See abstract on p. 163.

Determination of Boron in High-Temperature Alloys

A. H. JONES: 'Spectrophotometric Determination of Boron in High-Temperature Alloys by Quinalizarin Method.'

Analytical Chemistry, 1957, vol. 29, July, pp. 1101-5.

Boron in high-temperature alloys can be determined spectrophotometrically in the range 0·01-0·10 per cent. by using the characteristic colour of the boron-quinalizarin complex in strong sulphuric acid. No separations are necessary, because extraneous absorption due to coloured ions is compensated. Interference by titanium, which was revealed by the investigation reported, could prove serious at very low boron concentrations, but can be corrected if the titanium content of the alloy is known. Only concentrated sulphuric acid is used to obtain the correct acid concentration: titration and subsequent adjustment of the concentration are unnecessary. Results reported in the paper include determinations of boron in a cobalt-base alloy containing major amounts of chromium, nickel and molybdenum.

Corrigendum

Nickel Bulletin, 1957, vol. 30, Nos. 7-8, p. 135.

Right-hand column, paragraph 3

delete '(see p. 136)'

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks*.

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